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Polyphosphoric Acids and Their Ammonium Salts

L.V.Kubasova

This review examines the most important results of studies in the field of the chemistry of polyphosphoric acids and their ammonium salts. The chief physicochemical properties and characteristics of these compounds are described. Particular attention is paid to the problem of the preparation of condensed ammonium phosphates by both industrial and laboratory methods. The bibliography contains 113 references.

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1. INTRODUCTION

Ammonium phosphates are of considerable scientific and practical importance. Since they are compounds containing two of the most important plant nutrient elements—nitrogen and phosphorus—the various ammonium ortho-, pyro-, poly-, and metaphosphates can be used as nitrogen–phosphorus fertilisers, and some can be used as feedstuffs in animal husbandry and as technical salts. With respect to the total concentration of nutrient elements, the poly- and metaphosphates are more concentrated than the salts of orthophosphoric acid—monoammonium and diammonium phosphates. Agricultural-chemical experiments have shown that the phosphorus and nitrogen are just as effective in ammonium polyphosphates as in other water-soluble fertilisers. The high concentration of nutrients gives the polyphosphates a number of economic and agricultural-technical advantages and provides promising possibilities for their utilisation as highly effective concentrated fertilisers, but the technology of these compounds has been insufficiently developed. The extensive development of the electrothermal production of phosphorus and "thermal" phosphoric acids, and also the production of polyphosphoric acids by the evaporation of "extraction" phosphoric acid, are raising the problem of the conversion of these materials into various forms of concentrated fertilisers and technical salts.

Despite the urgency of the problem, published data on the chemistry and technology of dehydrated ammonium phosphates have not been reviewed. The present review therefore deals with the most important results of the studies of recent years in the field of the preparation and study of the properties of ammonium poly- and metaphosphates. The problems of the structural chemistry of the phosphates are not examined in detail, since this subject has been dealt with in depth in the monograph by van Wazer[1] and in reviews by Khodakov[2], Thilo[3], Britske and coworkers[4], and others.

2. CHEMISTRY OF POLYPHOSPHORIC ACIDS

As early as 1910, Balareff[5] noted that in the two-component $H_2O-P_2O_5$ system in the range of high concentrations of phosphorus(V) oxide (>72.4%), solutions consisting of a mixture of various phosphoric acids begin to form. This was one of the first suggestions that in this concentration range the 100% orthophosphoric acid formed does

not simply mix with the excess of phosphorus(V) oxide, but that a large quantity of other condensed forms of phosphate anions is gradually formed in the solution.

After the establishment of the existence of a large number of polymeric phosphates, the attention of research workers was drawn to the development of analytical methods for their separation and quantitative determination in the presence of one another. It was established that classical analytical methods based on precipitation make it possible to separate only the first three members of the homologous series of polyphosphates[6-8]. The concentration of all other polyphosphates was determined from the difference between the total concentration of phosphorus in the phosphate mixture and the phosphorus present in the ortho-, pyro-, and tripolyphosphates. This was attributed to the fact that the polymeric phosphate homologues have extremely similar chemical properties and tend to undergo hydrolysis to orthophosphate, so that attempts to separate them by precipitation are unsuccessful.

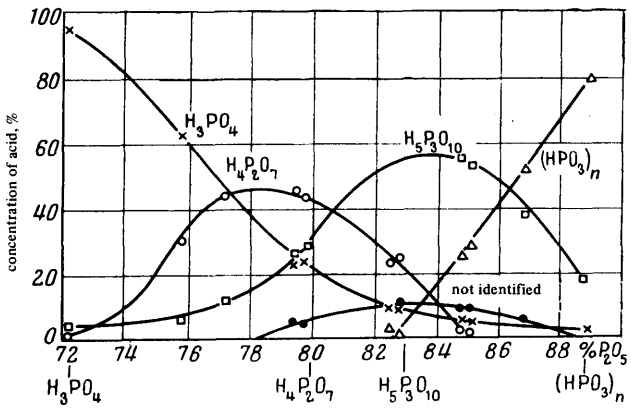


Figure 1. Composition of concentrated phosphoric acids.

Using the available analytical methods, Durgin and coworkers[9] established that phosphoric acids at high concentrations consist of mixtures of ortho-, pyro-, tripoly-, and other acids with different degrees of condensation. Later, Bell[10] detected regular features in the dependence of the production of a given phosphoric acid on the concentration of phosphorus(V) oxide in the solution (Fig. 1), namely that at concentrations in the range 72.4–85% P_2O_5 the solution always contains ortho- and pyrophosphoric acids, and in the range 72.4–88.7% P_2O_5 it also contains tripolyphosphoric acid $H_5P_3O_{10}$ in addition to these two acids. At a concentration greater than 83%, metaphosphoric acid appears in the polymeric form $(HPO_3)_n$.

Paper chromatography[11-15] has proved more successful for the separation of polyphosphate chains. Using this method, Huhti and Gartaganis[16] studied the compositions of phosphoric acids in the range 68.8–86.3% P_2O_5 and gave quantitative information on the concentration of phosphoric acids with different degrees of polymerisation in the mixture (Table 1). Unfortunately, even this most accurate method of polyphosphate analysis does not yet make it possible to separate polyphosphoric acids containing more than nine phosphorus atoms in the chain, so that the compositions of the acids with ratio $H_2O/P_2O_5 < 1.5$ have not yet been fully established. An interesting feature is that the author cited confirmed the previously noted observation[17] that liquid phosphoric acid with the theoretical composition of pure orthophosphoric acid (72.4% P_2O_5) contains 12.7% pyrophosphoric acid, the first detectable quantities of which begin to appear at 68.9% P_2O_5, and the composition of 100% orthophosphoric acid is achieved only on crystallisation.

Simon[18] considers that the rearrangement leading to partial condensation with the formation of free water and pyrophosphoric acid according to the equation

$$3H_3PO_4 \rightleftarrows H_4P_2O_7 + [H_3O]^+ + [H_2PO_4]^-,$$

takes place as a result of interaction within the three-dimensional structure and is associated with the presence of a large number of covalent bonds between hydrogen and oxygen atoms.

Table 1. Compositions of liquid polyphosphoric acids (according to Huhti and Gartaganis[16]).

Total P_2O_5 concentration	Ortho-	Pyro-	Tri-	Tetra-	Penta-	Hexa-	Hepta-	Octa-	Nona-	$(HPO_3)_n$
68.80	100	—	—	—	—	—	—	—	—	—
69.81	97.85	2.15	—	—	—	—	—	—	—	—
74.26	67.78	29.54	2.67	—	—	—	—	—	—	—
75.97	48.93	41.76	8.23	0.08	—	—	—	—	—	—
78.02	26.91	49.30	16.85	5.33	1.60	—	—	—	—	—
79.45	16.73	43.29	22.09	10.69	4.48	1.92	0.80	—	—	—
81.60	8.06	27.01	22.28	16.99	11.00	5.78	3.72	2.31	1.55	1.28
86.26	1.54	2.97	3.31	5.16	5.32	5.54	3.51	3.30	3.30	66.03

At the same time, studies of liquid phosphoric acids indicated that a definite molar ratio H_2O/P_2O_5 always corresponds to the same molar composition of the solution, which consists of a mixture of phosphoric acids with different degrees of condensation. This suggested that a given liquid polyphosphoric acid molecular composition expresses an equilibrium state between different structural units, molecules and molecular ions, which in the time taken for equilibrium to be established may break down and be re-formed repeatedly. There are many examples in organic chemistry of the rearrangement of molecular structures. This phenomenon for various processes has been studied in detail from the chemical viewpoint; in addition, a mathematical treatment of the molecular weight distribution in the intermediate compounds formed has been carried out[19] and has found extensive application for the description of unionised molecules as the Flory distribution function.

van Wazer and coworkers, following Flory, extended the theory of rearrangement to polyelectrolytes, that is ionised molecules such as those of the polyphosphoric acids, and derived an equation which makes it possible, for any given molar ratio H_2O/P_2O_5, to calculate the distribution of chains of different length[20]. It should be noted that recent work has shown that it is possible to carry out a more accurate quantitative analysis of polyphosphate compounds by means of computers.

Of the large numbers of known phosphoric acids, only a few have been identified and isolated in crystalline form. These are orthophosphoric acid hemihydrate ($H_3PO_4 \cdot 0.5H_2O$) and orthophosphoric (H_3PO_4), pyrophosphoric ($H_4P_2O_7$), and tetraphosphoric ($H_6P_4O_{13}$) acids. Other polyphosphoric acids have been obtained in the form of mixtures of acids

with different degrees of condensation, and form a series of compounds ranging from syrupy liquids, which crystallise slowly when kept, to amorphous glasses. The Americans Striplin and coworkers[21] of the TVA established the range of concentrations (75–76% P_2O_5) in which polyphosphoric acids are always produced in the form of syrupy liquids and do not crystallise on prolonged storage; in their opinion, this is due to the existence of a simple eutectic with the neighbouring region of the solutions, which have a strong tendency to undergo supercooling.

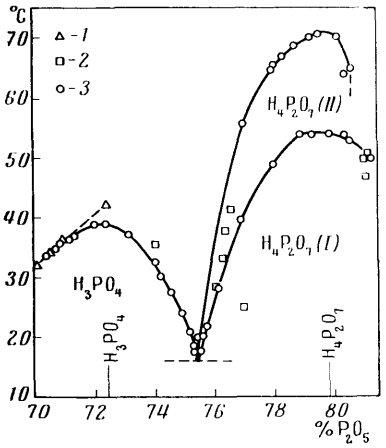


Figure 2. Fusion diagram of the $H_3PO_4-H_4P_2O_7$ system according to Refs. 23 (*1*), 24 (*2*), and 22 (*3*).

This suggestion was later confirmed by their colleague Wakefield and coworkers[22] in a study of phase changes in the $H_3PO_4-H_4P_2O_7$ system. The determination of the melting points of these acids, and the diagram constructed by the authors cited on the basis of the results obtained, show clearly the formation of a eutectic (16°) at a concentration of 75.4% P_2O_5 in phosphoric acid (Fig. 2). Moreover, the authors cited established the existence of two crystalline forms of pyrophosphoric acid, denoted (I) and (II). The ordinary metastable form (I) melts at 54.3°; the second form (II), the existence of which was confirmed by X-ray diffraction studies, melts at a higher temperature (71.5°). This form can be obtained by gradually heating the acid in form (I) above 54°, without stirring. All the acid, with the exception of a few crystals, melts, but further increase in temperature (from 60° to melting point) leads to the opposite phenomenon—all the liquid phase solidifies. The pyrophosphoric acid (II) obtained in this way is stable at room temperature. Transformation of one form of pyrophosphoric acid into the other in the solid phase was not observed. These results indicate that the melting point of 61° for pyrophosphoric acid, established in 1902 by Giran[25] and generally accepted since then reflects the melting point of a mixture of its two modifications.

In parallel with the study of the chemical compositions of polyphosphoric acids, a number of authors have determined the physical properties of these compounds. Particular attention has been paid to the study of such physicochemical characteristics as density and viscosity[9,26], a knowledge of which is very important for the industrial development of polyphosphoric acid production.

The experimental data on the density of thermal phosphoric acids over a wide range of concentrations have been treated mathematically and represented in the form of the equation given below, which makes it possible to find the temperature dependence of the density for acids at different concentrations

$$d = (0.7102 + 0.1617c) - (11.7 \cdot 10^{-4} - 6.00 \cdot 10^{-6}c)t,$$

where d is the density, g ml^{-1}; c the concentration (wt. % P_2O_5); and t the temperature, °C.

Workers from Monsanto[27] recommend a slightly simplified form of the equation for the concentration dependence of the density of the condensed acids

$$d = 0.0167(\%P_2O_5) + 0.66$$

for concentrations of phosphorus(V) oxide in the acid from 50% to 95%.

The viscosity of polyphosphoric acids was determined by Durgin and coworkers[9] in the range 71.8–77.1% P_2O_5 and by Kondratenko and Fedorchenko[28] in the range 65.2–74.6% P_2O_5. The results made it possible to establish the temperature dependence of the viscosity for a wide range of polyphosphoric acids as far as the azeotropic composition containing 92.4% P_2O_5.

Similar studies of the physicochemical properties of polyphosphoric acids obtained by the extraction method were carried out by Mal'tseva and coworkers[29,30], who were able to determine a number of thermochemical constants characterising the dilution of polyphosphoric acids; this is of considerable importance in the technology of polyphosphoric acids.

The industrial production of highly concentrated phosphoric acids is now carried out on the basis of the electrothermal process for the preparation of phosphorus and its oxidation, and on the basis of the production of extraction phosphoric acid.

Despite the fact that vacuum-evaporation, spraying, and other apparatus making it possible to increase the concentration of extraction phosphoric acids to 70% P_2O_5 [31-33] has been developed and introduced, the production of polyphosphoric acids by this method has not until recently found extensive industrial application. This is because the concentrated phosphoric acids obtained in this way in most instances are contaminated by traces of sulphuric acid, sesquioxides of iron and aluminium, etc.

In most instances, the direct method of preparing polyphosphoric acids in the electrothermal production of phosphorus is used. The production of polyphosphoric acid on a pilot-plant scale was first carried out by the TVA and in Japan[34,35]. The production scheme was as follows. The phosphorus(V) oxide vapour leaving the phosphorus combustion chamber was cooled to 460° and passed to an absorption tower, irrigated at 210–220° with concentrated 85% phosphoric acid. This high concentration of acid used for irrigation was necessary to obtain the maximal degree of absorption of phosphorus(V) oxide (99%). The concentration of acid leaving the tower was 87% P_2O_5. The proposed scheme required very rigorous observation of the temperature conditions of the absorption and the concentration of the absorbent. To avoid these technological difficulties, the same authors later proposed a new scheme for the production of polyphosphoric acid containing 76% P_2O_5,[20,36,37] according to which oxides of phosphorus containing small quantities of metaphosphoric acid at 600° were passed to a hydrating apparatus irrigated with water and dilute orthophosphoric acid. The resulting polyphosphoric acid was passed through a cooling channel into a

collector, and the unabsorbed phosphorus oxides in the form of a mist were trapped in an electrostatic filter or in a packed tower. Phosphoric acids at this concentration are extremely aggressive towards most metals, and the aggressive character increases considerably with increase in temperature to several hundred degrees, so that most of the apparatus (combustion chamber, hydration towers) had to be made of graphite or lined with acid-resistant brick.

Recently, the TVA has built a number of new plants for the production of polyphosphoric acid with increased concentration (~ 80% P_2O_5), [38] in which the old graphite equipment has been replaced by new stainless steel equipment.

In the Research Institute for Fertilisers and Insectofungicides, Postnikov and coworkers [39] have developed a new scheme for the preparation of thermal concentrated phosphoric acids (103–110% H_3PO_4). The authors rejected the old designs of plant with linings and changed to unlined metal equipment with water-cooled walls to remove the excess of heat and protect the metal from corrosion.

A number of authors have suggested a method involving the repeated rectification of a mixture of phosphoric acids and organic solvents to increase the concentration of these acids [40,41]. Recent work has shown that the best results are obtained by using such solvents as n-butanol, cyclopentanol, cyclohexanol, and 3-methylbutanol, which make it possible to reach a concentration of phosphorus(V) oxide in the acids equal to 77.8–93.8%. This method has not yet found extensive industrial application and is used only when necessary to prepare small quantities of concentrated polyphosphoric acid.

For preparative purposes, polyphosphoric acids can be obtained from the corresponding sodium polyphosphates by means of ion exchange resins in the H-form [42-47] or by adding phosphorus(V) oxide to pure orthophosphoric acid [16].

3. CHEMISTRY AND TECHNOLOGY OF DEHYDRATED AMMONIUM PHOSPHATES

The first papers on the chemistry of the salts of the above polyphosphoric acids appeared more than one hundred years ago. Graham [48], Fleitmann and Henneberg [49], Tammann [50], and a number of other workers developed methods of preparation and described a number of properties of polymeric phosphates of sodium and to a smaller extent potassium. Since inorganic chemical theory at that time was not well developed and sufficiently reliable analytical and physicochemical methods of study were not available, the authors cited made a number of errors in the nomenclature of the condensed phosphates, and this acted as a source of confusion and incorrect ideas regarding the structures of some of these compounds.

A systematic detailed study of the methods of preparation, properties, and structures of various oxygen compounds of phosphorus was undertaken about the middle of the twentieth century. Important work on the structural chemistry of the dehydrated phosphates and their classification and systematisation has been carried out by van Wazer, Thilo, Britske, and Khodakov and coworkers.

The large amount of physicochemical data obtained in the study of dehydrated phosphates, and a number of theoretical generalisations, have led these authors to the conclusion that there exist homologous series of phosphates, from the monomers to the higher members of the series, formed by the sharing of oxygen atoms between the structural units, each of which consists of a tetrahedral group of four oxygen atoms around a central phosphorus atom. Several different structural types can be distinguished in the polymeric phosphates, depending on the way in which the individual PO_4 tetrahedra are joined by the oxygen atoms shared by neighbouring tetrahedra, that is depending on the number of oxygen atoms corresponding to each PO_4 tetrahedron.

Polyphosphates —a homologous series of salts, the anions of which consist of PO_4 tetrahedra joined to one another by oxygen atoms in continuous chains of different length.

Metaphosphates $(MPO_3)_n$ are phosphates with anions having a ring structure.

Branched or network phosphates are compounds containing a greater or smaller number of "quaternary" phosphorus atoms, joined to other phosphorus atoms through three oxygen atoms. Van Wazer considers that there are several forms of structural block (point of branching, central and terminal groups) from which all these types of dehydrated phosphate can be constructed by different relative arrangements. By combining all these structural blocks in the most varied ways, it is possible to obtain a wide variety of hypothetical formulae for the condensed phosphates. The total number of structures formed in this way, however, does not always agree with the number actually existing, since the possibility of existence of a given structure is determined by steric factors (the strain in the P–O–P bonds, the size of the valency angles, etc.).

On the basis of a calculation of the total number of bonds in a given phosphate, van Wazer [51] proposed a method for calculating the formulae of phosphates of different structural types, according to which chain phosphates can be described by the formulae $M_{n+2}P_nO_{3n+1}$ and $M_nH_2P_nO_{3n+1}$, where n is the degree of condensation. Ring phosphates have the formula $M_nP_nO_{3n}$. As $n \to \infty$, the general formula of the chain polyphosphates $M_{n+2}P_nO_{3n+1}$ approaches that corresponding to the metaphosphate composition $(MPO_3)_n$, so that the last formula is the limiting formula for both chain and ring phosphates. Thus the term "metaphosphate", covering a wide range of polymeric phosphates with the composition $(MPO_3)_n$ with both chain and cyclic structures, still appears in the literature.

Despite the fact that various physicochemical methods for the study of polymeric compounds are now known and widely employed (paper chromatography, infrared spectroscopy, X-ray diffraction), the determination of the structures and molecular weights of various condensed phosphates presents considerable difficulty.

Nuclear magnetic resonance (NMR) has proved extremely effective for the qualitative determination of the compositions of mixtures of various phosphates and the investigation of their structures. The use of this method became possible because the resonance peaks in the NMR spectra of phosphates result from the presence, in the phosphate anions, of the so-called central and terminal groups, the concept of which was introduced by van Wazer. It has been established that a central group in a chain is equivalent to a central group in a ring, and also that terminal groups exhibit identical bond characteristics, irrespective of the chain length [52-54].

The NMR spectra of the anions of chain phosphates, given in Fig. 3, show clearly the change in the character of the spectrum with change in the ratio of terminal and central groups in the anion. Thus the spectrum of the pyrophosphate reflects the presence of only terminal

groups, whereas the spectrum of tripolyphosphate reveals a central group in addition. It can readily be seen that in the spectrum of the tripolyphosphate the peak of the terminal group is split to form a doublet, and the peak of the central group is a triplet. This is not accidental, but is related to the nature of the bonds in the terminal and central groups in the tripolyphosphate: each terminal group is joined to one central group, and each central PO_4 group to two terminal groups.

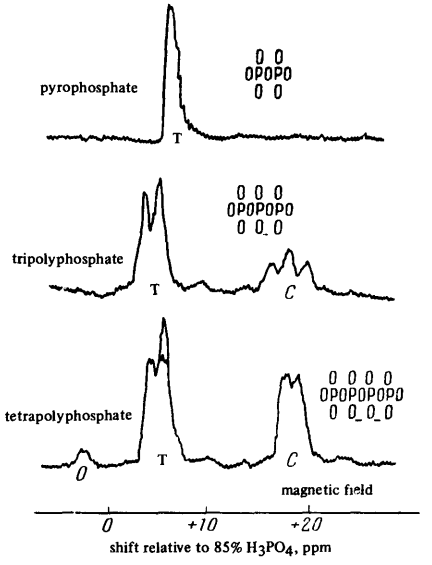


Figure 3. NMR spectra of polyphosphate anions; T—peaks due to terminal groups; C—peaks due to central groups; O—peaks due to orthophosphate.

The NMR spectrum of the tetrapolyphosphate anion in a solution of crystalline ammonium tetrapolyphosphate reflects the presence of terminal and central groups; the peaks reflecting these groups are split to form doublets, proving that this anion has a linear structure.

A characteristic feature is that the ratio of terminal to central groups can be estimated by comparing the areas under the corresponding peaks (2 : 1 for the tripolyphosphate and 2 : 2 for the tetrapolyphosphate).

All the NMR spectra of different metaphosphate specimens showed the presence of exclusively central groups, proving conclusively the original structure of the metaphosphate anions.

Unfortunately, the NMR method has not yet been sufficiently fully developed for the quantitative analytical determination of mixtures of phosphates.

The existence of "inorganic rings" with six members (trimetaphosphates) and eight members (tetrametaphosphates) has suggested the possible production of different steric configurations in these compounds, analogous to that observed in the chemistry of organic cyclic compounds (cyclohexane, decalin, etc.).

The most detailed studies from the viewpoint of stereochemistry have been made for only two ammonium salts, the trimetaphosphate $(NH_4)_3P_3O_9$ and the tetrametaphosphate $(NH_4)_4P_2O_{12}$, which are comparatively stable in aqueous solution and do not undergo immediate hydrolysis. It has been found that the molecules of these compounds can in fact exist in two different geometric configurations: the boat form (a) and the chair form (b) (Fig. 4).

Figure 4. Configuration of the molecules of ammonium tri- and tetrametaphosphates: *a*) boat form; *b*) chair form.

As a consequence of the difference in various physical and chemical properties of these geometric isomers, it is comparatively easy, by fractional crystallisation or paper chromatography, to separate their mixtures and identify each of the forms for more detailed study. Thus Romers and coworkers[55] made an X-ray diffraction study of one of the isolated isomers of ammonium tetrametaphosphate, with the chair conformation. They were able to establish the presence of regular PO_4 tetrahedra in the metaphosphate anions; the phosphorus atoms are not situated at the centres but are displaced away from the oxygen atoms common to two tetrahedra. The authors cited attributed this to the influence of hydrogen bonds between the unshared oxygen atoms of the PO_4 groups and the nitrogen atoms of the ammonium ions. This explanation has been disputed by van Wazer, since the displacement of the phosphorus atoms may be due to the presence of negative charges on the unshared oxygen atoms as a consequence of the ionisation of the phosphate anion.

This is only one of many examples indicating that many problems of the stereochemistry of condensed phosphates are still unsolved (methods for proving spatial configurations, and their separation), and for various extremely interesting problems, such as the presence of a conformation or the interconversion of rings etc., there is almost no published information.

The possibility of extensive and varied applications of polymeric phosphates in the national economy has drawn the attention of research workers to not only the chemistry but also the technology of these compounds. Attempts have been made to find simpler and more rational methods for their preparation. Phosphates with polymeric compositions were first prepared not by neutralising the corresponding polyphosphoric acids but by the thermal dehydration of acid salts of orthophosphoric acid:

$$n\,MH_2PO_4 \rightarrow (n-1)\,H_2O + M_nH_2P_nO_{3n+1},$$

and for this reason they have been called dehydrated phosphates.

This comparatively simple method has found extensive application for the preparation of polyphosphates of sodium, potassium, lithium, and other elements, namely those for which the acid orthophosphates do not undergo any changes other than removal of water of constitution in the temperature range of dehydration. These compounds have been studied in most detail. (The results of studies published up to 1956 have been reviewed by van Wazer in the first volume of the monograph "Phosphorus and its Compounds".)

There is very little information on the ammonium salts of polyphosphoric acids. This is apparently due to the fact that the method of thermal dehydration, widely employed in practice for the preparation of poly- and metaphosphates, cannot be used for the ammonium salts, since with increase in temperature, ammonium hydrogen orthophosphates decompose with the liberation of ammonia before dehydration takes place.

In 1955, Thilo and Grunze[56] investigated the thermal dissociation of monoammonium phosphate in order to study the reaction products with maximal degree of dehydration. They showed that the decomposition of monoammonium phosphate on heating takes place in stages according to the reactions

$$NH_4H_2PO_4 \xrightarrow[\text{up to } 140^\circ]{-NH_3} NH_4H_2PO_4 + H_3PO_4 + NH_3$$

$$NH_4H_2PO_4 \xrightarrow[140-190^\circ]{-NH_3;\ -H_2O} (NH_4)_n H_2P_nO_{3n+1};\ (NH_4, H)_{n+2}P_nO_{3n+1}$$

$$(NH_4)_n H_2P_nO_{3n+1} \xrightarrow{} H_{n+2}P_nO_{3n+1}$$

$$(NH_4)_n H_2P_nO_{3n+1} \xrightarrow[200-300^\circ]{} (NH_4PO_3)_n$$

$$(NH_4PO_3)_n \xrightarrow[300^\circ]{-NH_3} (HPO_3)_n$$

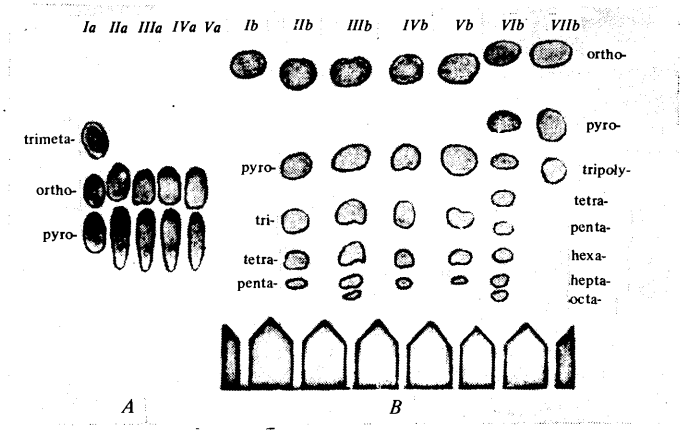


Figure 5. Paper chromatogram for the products of the dehydration of $NH_4H_2PO_4$ (*A*—chromatography in ammoniacal solution; *B*—chromatography in acid solution); *Ia*) mixture of standards (trimeta-, ortho-, and pyrophosphates), *Ib*) $NH_4H_2PO_4$ after heating for 24 h at 140°, *II*–*VII a* and *b*) products of the dehydration of $NH_4H_2PO_4$ at 150, 160, 170, 200, 230, and 250° (for 24 h).

From this it follows that the dehydration of monoammonium phosphate, which begins at ~ 140°, is accompanied by the liberation of ammonia. Using paper chromatography to analyse the dehydration products, Thilo and Grunze established that in the range 140–190° a mixture of oligophosphates with the composition $(NH_4)_nH_2P_nO_{3n+1}$, with degree of condensation n in the range 1–5, is formed. On further heating, the greater part of the mixture is converted, with loss of ammonia, into polyphosphoric acids with higher molecular weight, and a very small fraction is converted into a water-insoluble macromolecular crystalline ammonium polyphosphate (Fig. 5). Above 300°, this salt also is unstable, and decomposes with the liberation of ammonia to form polyphosphoric acid.

Analogous phenomena were observed by Japanese workers in a study of the possibility of preparing ammonium polyphosphates by the thermal degradation of acid ammonium salts of orthophosphoric acid. Unlike Thilo, Kobayashi[57] was able, not merely qualitatively, to characterise the dehydration of monoammonium phosphate at various temperatures from 175° to 300° ± 5° with heating for different periods of time (maximal duration of dehydration 25 h). Data on the ratios of pyro- and tripolyphosphates and phosphates with higher molecular weight, and also on the quantity of undehydrated orthophosphate, were obtained by ion exchange chromatography on Dowex-1-X8 resin (KCl solutions with different concentrations were used as eluant). It was established that even at 300°, dehydration is not complete, and the final product contains from 15% to 5% P_2O_5 in the ortho-form, relative to its total concentration, depending on the duration of heating. Increase in the duration of heating at any temperature leads to more complete dehydration, but the relationships for the formation of pyro- and tripolyphosphates and other dehydrated forms of phosphate are different. At 175, 200, and 225°, a general tendency for the dehydrated forms of the phosphates to increase with increase in the duration of dehydration is observed, whereas at higher temperatures (260 and 300°), at definite stages of the dehydration, the quantity of pyro- and tripolyphosphates formed reaches a maximum and then gradually decreases, with a corresponding increase in the quantity of polyphosphates with higher molecular weight.

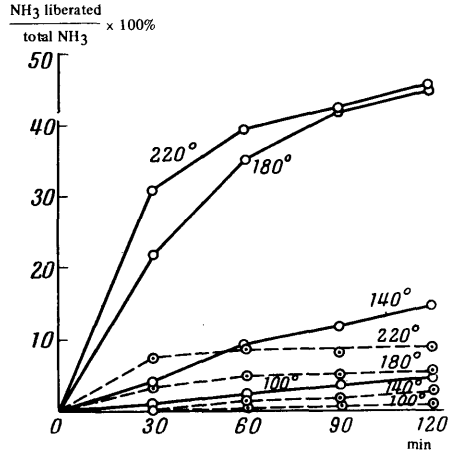


Figure 6. Dependence of the liberation of ammonia on the time for which diammonium phosphate and ammonium polyphosphate are heated at various temperatures: continuous lines—diammonium phosphate; broken line—polyphosphate.

The chemical compositions of the products show that in fact the dehydration of monoammonium orthophosphates is accompanied by appreciable loss of ammonia; the concentration of ammonia gradually decreases from 16% at 175° to 11% at 300° (heating for 25). The formation of acidic ammonium polyphosphates ($NH_4 < H$) is also confirmed by the fact that solutions of the specimens studied had an acidic reaction (pH 2.5–4.0).

It should be noted that the ammonium polyphosphates themselves decompose with the liberation of ammonia with much greater difficulty than the original salts of orthophosphoric acid[58]. This is clearly confirmed by data obtained in a study of thermal dissociation up to 220° over a period of 2 h for diammonium phosphate and ammonium polyphosphate with an average degree of condensation n = 7–8 (Fig. 6). Above 140°, diammonium hydrogen phosphate is converted into a mixture containing varying quantities of diammonium pyrophosphate and triammonium tripolyphosphate[59].

To obtain ammonium phosphates with the maximal degree of dehydration, corresponding to the chemical composition $(NH_4PO_3)_n$, Vol'fkovich and Kubasova[60] proposed a method for the thermal dehydration of ammonium hydrogen orthophosphates under a pressure of gaseous ammonia.

The use of gaseous ammonia in the dehydration made it possible to find conditions in which the pressure of ammonia vapour during the decomposition is balanced by the ammonia pressure created above the original salt, and the dehydration proceeds without the loss of ammonia (at an approximately constant molar ratio NH_3/P_2O_5), with a continuously increasing degree of dehydration, that is with a decrease in the molar ratio H_2O/P_2O_5 in the dehydration products. The greater part of the water of constitution is removed from monoammonium orthophosphate in the range 275–325°, after which the rate of dehydration decreases; the composition of the products approaches that of macromolecular polyphosphates of the type $(NH_4PO_3)_n$.

Unfortunately, the production of ammonium polyphosphates by thermal dehydration must at present be regarded as a preparative method, since all the experiments were carried out in laboratory apparatus by batch methods. The pilot-plant or industrial introduction of this method of preparation requires the development of equipment which would make possible a continuous process.

Recently, Kobayashi[61] described a study of the kinetics of formation of condensed ammonium phosphates in a continuous process involving the reaction of thermal phosphoric acid with ammonia. The experimental assembly is illustrated in Fig. 7. The starting materials (phosphoric acid and ammonia) were introduced into the first reaction vessel, which was heated by external and internal heaters to 230° or 250°, after which phosphoric acid, previously heated to 100° by heat exchange with steam leaving the reaction vessel, was introduced into the reaction vessel. Contact between the phosphoric acid and the liquid in the reaction vessel led to intensive volatilisation with the removal of a large proportion of the water, leaving a salt melt in the reaction vessel. With mixing (rate of stirring 200 rev min^{-1}) the phosphoric acid reacts with ammonia (simultaneous ammonium salt formation and dehydration), as a result of which the level of liquid in the reaction vessel increases and the product is removed continuously from the reaction vessel through an outlet.

For $(NH_4)H_2PO_4$ heated in a batch process, the rates of formation of the individual salts (r_2 for pyrophosphate, r_3 for tripolyphosphate, and r_m for the average polyphosphate) were calculated by substituting the apparent rates of formation in the reaction rate equation derived on the basis of the known mechanism of complex formation. The following values were obtained for the range 230–250°: $r_2 = 2 \times 10^{-2} - 1 \times 10^{-3}$ mole min^{-1}, $r_3 = 5 \times 10^{-3}$ mole min^{-1}, and $r_m = 1 \times 10^{-3} - 1 \times 10^{-4}$ mole min^{-1}.

The rates of the reaction between phosphoric acid and ammonia were determined from the kinetic equation applicable to continuous processes in bulk apparatus. In these experiments it was established that the concentration of condensed phosphates in the final product decreases with increase in the input of starting materials. The reaction rate increases, however. Thus for example at a reaction temperature of 250°, increase in the input of phosphoric acid by increasing the concentration from 30% to 50% (calculated as P_2O_5) increases the reaction rate from 0.385 kg h^{-1} $litre^{-1}$ to 0.651 kg h^{-1} $litre^{-1}$.

The products contained 10–12% nitrogen and 62–67% P_2O_5 and had an acidic reaction. For this reason, the treatment with ammonia was repeated. The condensed phosphates obtained in this way contained 13–15% nitrogen and 65% P_2O_5. The degree of conversion of $(NH_4)H_2PO_4$ into $(NH_4 + H)_{n+2}P_nO_{3n+1}$ (where n = 2–10) was 60–80%.

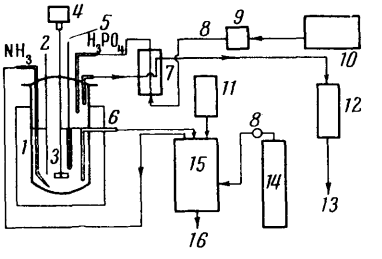


Figure 7. Diagram of the laboratory apparatus for the preparation of condensed ammonium phosphates[61]: *1*) external heater; *2*) thermistor; *3*) first reaction vessel; *4*) motor with stirrer; *5*) heating element; *6*) removal of product; *7*) heat exchanger; *8*) flow meter; *9*) pump; *10*) phosphoric acid tank; *11*) vessel for added salts; *12*) cooler; *13*) water; *14*) ammonia cylinder; *15*) second reaction vessel for repeated treatment with ammonia; *16*) final product.

The experiments showed that the ammonium polyphosphate obtained can be mixed with a number of salts containing various nutrient elements, for example with potassium chloride during the repetition of the treatment with ammonia, and this is of interest for the preparation of complex fertilisers.

Various dehydrated ammonium phosphates can also be prepared by ion exchange from solutions of the polymeric phosphates of other cations, followed by treatment of the polyphosphoric acid solutions with ammonia and precipitation of the crystalline salts with ethanol or acetone[62,63].

A number of papers describing the properties of condensed ammonium phosphates, prepared by ion exchange, have been published[64,65]. Unfortunately, some contain inaccurate data, since they describe not the pure salts but their mixtures. Ammonium pyro- and tripolyphosphates have been most fully characterised in a review by Frazier[66], who described the methods of preparation and the crystallographic properties of six pyrophosphates: $(NH_4)_2H_2P_2O_7$ (monoclinic and orthorhombic), $(NH_4)_3HP_2O_7$, $(NH_4)_3HP_2O_7.H_2O$, $(NH_4)_4P_2O_7$, $(NH_4)_4P_2O_7.H_2O$, and six tripolyphosphates: $(NH_4)_3H_2P_3O_{10}$, $(NH_4)_3H_2P_3O_{10}.H_2O$, $(NH_4)_4HP_3O_{10}$, $(NH_4)_9H(P_3O_{10})_2.2H_2O$, $(NH_4)_5P_3O_{10}.H_2O$, and $(NH_4)_5P_3O_{10}.2H_2O$. All these salts were prepared from recrystallised reagents or obtained as solid phases in the

determination of solubility according to Farr and Fleming[67] in the $NH_3-H_4P_2O_7-H_2O$ and $NH_3-H_5P_3O_{10}-H_2O$ systems. To obtain reliable results, the authors cited prepared the original condensed ammonium phosphates by three methods. The passage of solutions of $Na_4P_2O_7$ or $Na_5P_3O_{10}$ through Amberlite IR-120 resin which had been treated with acid gave solutions of the corresponding acids, which were immediately treated with ammonia and evaporated in a vacuum. To prevent hydrolysis, all these operations were carried out below 10°.

Ammonium tripolyphosphates were prepared by fractional crystallisation of the products obtained by treating thermal superphosphoric acid (79–82% P_2O_5) with ammonia. $(NH_4)_5P_3O_{10}\cdot H_2O$ was purified by recrystallising eight times. Other tripolyphosphates were obtained by lowering the pH of solutions of this salt with Amberlite IR-120 resin and then treating the eluate with ethanol. The salt frequently separated in the form of an oily liquid; a seed crystal was added to bring about crystallisation.

Ammonium pyrophosphate $(NH_4)_4P_2O_7$ was prepared by treating aqueous solutions or suspensions of calcium ammonium pyrophosphates with ammonium fluoride. This salt was recrystallised and used for the preparation of more acidic ammonium pyrophosphates.

A recently published paper by French workers[68] on the isolation of a new ammonium salt with mixed orthophosphate and pyrophosphate anions $(NH_4)_2H_5(PO_4,P_2O_7)$, with melting point 93° ± 1°, is of interest. According to the authors cited, this acidic ammonium phosphate is a new compound and should not be regarded as an intermediate product of the thermal dehydration of the orthophosphate with formation of the pyrophosphate.

Frazier[66], and later other workers[69], paid particular attention to the problems of the stability of ammonium pyro- and tripolyphosphates; this is of direct interest in the study of the possibility of using condensed ammonium phosphates as highly concentrated liquid and solid nitrogen-phosphorus fertilisers. Thus it has been established that tetrasubstituted ammonium pyrophosphate, unlike the analogous potassium and lithium salts, does not condense in the presence of acetic anhydride at room temperature, but at higher temperatures it forms a mixture of linear phosphates[70]. The solubility of ammonium pyro- and tripolyphosphates and the phase changes in the $NH_3-H_4P_2O_7-H_2O$ and $NH_3-H_5P_3O_{10}-H_2O$ systems were studied by Farr and coworkers[71].

Ion exchange has been used to isolate not only ammonium polyphosphates with a chain structure, but also ammonium salts with the metaphosphate composition containing phosphate ions with ring structures—ammonium trimeta- and tetrametaphosphates; this is attributed to the stability of trimeta- and tetrametaphosphoric acids in aqueous solutions. It has been established[73] that ammonium trimetaphosphate is stable as far as 100°, but on further heating at 120–180° it undergoes hydrolysis, absorbing moisture from the atmosphere, and is converted into a mixture of acidic "oligophosphates" with the composition $(NH_4)_nH_2P_nO_{3n+1}$. Above 180° these compounds also decompose with the liberation of ammonia, with the formation of polyphosphoric acids containing traces of macromolecular ammonium polyphosphate.

Chromatographic analysis (Fig. 8) showed that the thermal dissociation of ammonium tetrametaphosphate takes place analogously only if the salt is heated gradually over a prolonged time interval. If the heating is rapid, over a period of 2–3 h, a macromolecular crystalline ammonium polyphosphate containing an anion with a chain structure is formed.

The properties of crystalline ammonium polyphosphate with the composition $(NH_4)_{n+2}P_nO_{3n+1}$, where n ~ 50 or more, have been described[66]. This salt was prepared from the product obtained by treating superphosphoric acid (83–84% P_2O_5) with ammonia, by crystallisation as the transparent ammonium polyphosphate gel dissolved. The crystals, when washed with acetone and dried in air, are stable at room temperature and remain crystallographically unchanged when heated at 105° for 48 h. This polyphosphate does not show a great similarity to Madrell's or Kurrol's salts as far as optical properties are concerned. Its infrared spectrum is similar to that of Kurrol's salt and is quite unlike that of metaphosphates containing phosphate anions with a cyclic structure.

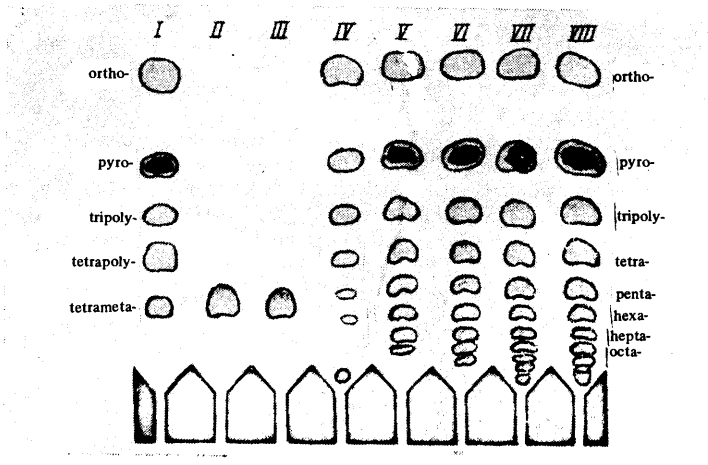
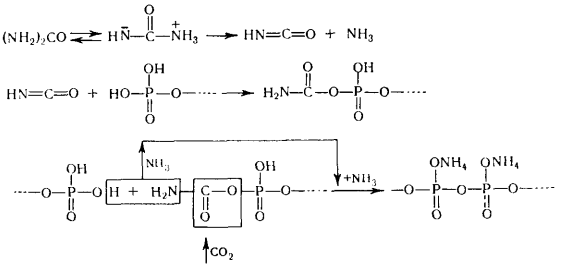


Figure 8. Paper chromatogram for the products obtained by heating ammonium tetrametaphosphate. Bands: *I*) standards (ortho-, pyro-, tripoly-, tetrapoly-, and tetrametaphosphates); *II*) $(NH_4)_4P_4O_{12}$; *III – VIII*) products obtained by heating $(NH_4)_4P_4O_{12}$ for 24 h at 100, 150, 200, 250, and 280°.

In recent years a number of papers reflecting the search for new methods for the preparation of ammonium polyphosphates from various phosphoric acids, including the use of urea as nitrogen-containing reagent, have been published. Phosphoric acids react with urea in solution and in the melt to give complex compounds—urea phosphates $(NH_2)_2CO.H_3PO_4$.[74–76] Japanese workers have established that reaction between phosphoric acid and urea begins at temperatures close to the decomposition temperature of urea with the formation of ammonium polyphosphate[77–79]. The authors cited paid particular attention to the influence of temperature, the concentration of the original phosphoric acids, and the quantitative component ratios, on the composition and properties of the compounds obtained. As original phosphoric acids they chose liquid polyphosphoric acids, containing 71.2–87.8% P_2O_5. The quantities of urea taken for the reaction were calculated from the given ratios $(NH_2)_2CO:P_2O_5$, equal to 1–4. It was found that the reaction of the polyphosphoric acids with urea in the ratio $P_2O_5:(NH_2)_2CO = 1:2$ even at 80° gives a sufficiently high yield of ammonium polyphosphates, although part of the urea remains unreacted (up to 14.6%

with acid containing 71.2% P_2O_5 and about 4% with acid containing 87.8% P_2O_5).

The reaction proceeds to the greatest extent at 140° – 160°. The isocyanuric acid liberated, in the opinion of the authors cited, indicates that the following reaction mechanism is most probable:



The small quantities of isocyanuric acid present can be readily removed by filtration, and the ammonium polyphosphate formed is removed from the solution by adding ethanol. The results in Table 2 show that the quantity of unreacted urea and isocyanuric acid liberated depends chiefly on the quantitative original component ratios.

Table 2. Compositions and qualitative ratios of the products of the reaction of polyphosphoric acids and urea at 140°.

Basic data on the reaction	Concn. of P_2O_5 in the original polyphosphoric acid, wt.%						
	83.0			87.6			
Starting materials							
Polyphosphoric acid, g	50.0	50.0	50.0	50.0	50.0	50.0	50.0
Urea, g	23.4	35.1	46.8	18.5	37.0	55.5	74.6
Ratio $(NH_2)_2CO:P_2O_5$	1.3	2.0	2.6	1.0	2.0	3.0	4.0
Reaction products							
Ammonium polyphosphate							
$(NH_4)_2O$, %	26.2	26.7	27.2	20.3	26.4	27.2	27.1
P_2O_5, %	72.5	72.1	72.3	60.9	73.0	73.1	72.2
$(NH_4)_2O:P_2O_5$ molar ratio	0.98	1.01	1.03	0.91	0.93	1.02	1.03
Average chain length	14.4	17.3	14.6	16.2	26.4	17.3	16.8
pH (1% solution)	6.1	6.4	6.2	2.3	5.9	6.2	6.2
Unreacted urea, %	3.3	10.2	16.6	1.1	3.1	12.7	17.9
Isocyanuric acid, %	3.0	3.7	3.0	5.5	14.5	18.0	9.0

The condensation mechanism of formation of ammonium polyphosphates has been proved by infrared spectroscopy [80,81]. All the polyphosphates obtained in this way contained anions with a chain structure. The average length of the chains in the anions was determined by potentiometric titration of the weakly acidic terminal OH groups. The quantitative ratio of phosphate anions with different degrees of condensation was established chromatographically. Phosphoric acid (61–69% P_2O_5) gave ammonium polyphosphates with a relatively short chain, and polyphosphoric acid (80–88% P_2O_5) gave compounds with a much longer chain.

The formation of condensed phosphates when monoammonium phosphate and urea are heated together (110–120°) was established by Vol'fkovich and coworkers [82], who made a physicochemical study of the production of nitrogen–phosphorus fertilisers from polyphosphoric acids and and intermediate product of the preparation of urea.

Industrial methods for the preparation of ammonium polyphosphates are based on the treatment with ammonia, a reaction which has been well studied for orthophosphoric acid. To increase the extent of the reaction of ammonia with the polyphosphoric acids, many authors have proposed that the process be carried out, as in Soviet work, under a pressure of gaseous ammonia [83-87]. Thus Getsinger and coworkers studied the reaction of ammonia with polyphosphoric acid containing 76% P_2O_5, under an ammonia pressure of 0.7–21 atm at 170–230°.

The neutralisation was carried out in a stainless steel reaction vessel with turbine stirrer. The reaction is very exothermic, so that to prevent decomposition of the final products, some of the heat of the reaction was removed by circulating water. The ammonium polyphosphates were obtained in the molten state. To improve the physical properties and in particular to decrease the hygroscopic character of the polyphosphates, the melt was granulated. Analysis of the final products showed that they consist of a mixture of ammonium polyphosphates with different degrees of dehydration, the chief components being monoammonium orthophosphate and the neutral and acidic ammonium pyrophosphates $(NH_4)_4P_2O_7$ and $(NH_4)_3HP_2O_7.H_2O$. The composition of the products varied from 16-61-0† to 18-69-0, depending on the conditions of treatment with ammonia (temperature, pressure, and duration of interaction of the reagents).

To develop technological conditions for the production of ammonium polyphosphates, experiments were carried out on a pilot-plant assembly with thermal phosphoric acid (77% P_2O_5) and highly concentrated extraction phosphoric acid (72% P_2O_5). [88] The treatment of the phosphoric acids with gaseous ammonia was carried out in an autoclave similar to that described earlier, at an automatically controlled pressure of 1.75–2.5 atm. The ammonium polyphosphate melt removed from the reaction vessel at 190° was passed to a horizontal two-roller mixer-granulator, in which it was simultaneously cooled to 60–100°, depending on the concentration of phosphoric acid used. The final solid product contained 14–15% N and 59–61% P_2O_5 (total), of which 40–50% P_2O_5 was in the dehydrated form.

According to a patent of Hignett and Getsinger [89], ammonium polyphosphates are obtained in the form of a solidified melt from gaseous ammonia and polyphosphoric acid (74–85% P_2O_5) or concentrated extraction acid (65–75% P_2O_5) at a pressure of 0.7–7 atm and 173–196°. The product was a mixture $(NH_4 + H)_{n+2}P_nO_{3n+1}$, with n = 2–10, containing 16% N and 61% P_2O_5.

In recent years, laboratory experiments have been carried out in the USSR, in the Samoilov Fertiliser Research Institute, on the preparation of solid ammonium polyphosphate by the treatment of polyphosphoric acids with ammonia without pressure, and it has been shown that it is possible in principle to obtain a product with good physical properties [90].

The TVA has developed on the laboratory scale a two-stage process [91] for the preparation of ammonium polyphosphate from extraction phosphoric acid (containing 55% P_2O_5) by neutralisation at an elevated temperature (121–155°). To prevent solidification of the ammonium polyphosphate melt, the temperature in the second neutralisation vessel was kept at an even higher level (~ 246°). The melt, containing ~ 50% phosphate in the polyphosphate form, was transferred to a screw granulator together with the recycle. The final product contained 11–12% N and 63–59% P_2O_5.

The direct reaction of phosphorus(V) oxide with ammonia might be of interest for the preparation of ammonium phosphates with the maximal degree of dehydration.

† Conventional symbols for the composition of the fertilisers: 16% N; 61% P_2O_5; and 0% K_2O.

This reaction has been known for a long time and has been studied by many workers[92-96]. It has been established that, irrespective of the conditions of the reaction, the production of (P–O–P) bonds and the production of (P–NH–P) bonds in the final products are equally probable, and this leads to the formation of a mixture of nitrogen-phosphorus compounds with different compositions, such as: diamidopyrophosphoric acid $P_2O_3(NH_2)_2(OH)_2$, diammonium monoamidophosphate $P_2O_3(ONH_4)_2(NH_2)(OH)$, or the ammonium salt of a polyphosphoric acid in which the phosphorus atoms are joined not only through oxygen atoms but also through imido-groups (NH).

Thus ammonium poly- or metaphosphates have not yet been obtained in the $P_2O_5-NH_3$ system. The formation of dehydrated ammonium phosphates of this kind should be expected in the $NH_3-P_2O_5-H_2O$ system.

A thermodynamic calculation by Britske and Dunaev[92] confirmed the possibility of obtaining ammonium poly- and metaphosphates in acceptable yield by the gaseous-phase reaction of phosphorus(V) oxide, ammonia, and water vapour; the formation of phosphates containing imido- and amido-groups is not excluded. The characteristics and composition of the products obtained in this ternary system depend not only on the $NH_3 : P_2O_5 : H_2O$ ratio, temperature, and duration of the interaction between the components, but also on a number of other factors, including the order in which the components are introduced.

A continuous process for the preparation of dehydrated ammonium phosphates in stages, carried out on a pilot-plant assembly by Stinson and coworkers[97], is apparently of technological interest. Phosphorus is burned in a stainless steel vessel at 370–405°. The phosphorus(V) oxide vapour produced is directed by means of a stream of dry air to a reaction vessel in which the first stage—the reaction of the phosphorus(V) oxide with gaseous ammonia—is carried out at 400–540°. Change in the temperature of the reaction within the range indicated, and the quantity of air used, had no influence on the properties of the intermediate products. These consisted of a mixture of various amido- or imido-derivatives of phosphoric acids with different degrees of dehydration. To obtain the final product with the metaphosphate composition, the second stage was carried out; this involved the treatment of the resulting mixture of intermediate products with steam in a rotating drum. This high-temperature hydrolysis leads finally to the formation of a product exhibiting good physical properties, in that it is relatively non-hygroscopic and is readily granulated. 70–75% of this product consisted of macromolecular ammonium polyphosphate $(NH_4PO_3)_n$ containing 16–19% nitrogen and 74–79% phosphorus(V) oxide. The remaining fraction of the product consisted of complex nitrogen-phosphorus compounds, the nature of which was not studied. From the equations for the reactions which may take place in the process, however:

$$P_4O_{10} + 4NH_3 = 2PN(OH)_2 + 2H_2O$$
$$PN(OH)_2 + H_2O = NH_4PO_3$$
$$PN(OH)_2 + NH_3 = PN(OH)ONH_4$$

the authors cited conclude that 10–15% consisted of $PN(OH)ONH_4$ and 10–20% of $PN(OH)_2$. Vol'fkovich and coworkers[98,99] in the Scientific Research Institute for Fertilisers and Insectofungicides and Moscow State University carried out laboratory studies on the preparation of phosphamic compounds from P_2O_5 and NH_3 in order to produce fertilisers not bound by soils.

Japanese workers[100-103] have also studied nitrogen-phosphorus compounds formed in the $P_4O_{10}-NH_3$ and $P_4O_{10}-NH_3-H_2O$ systems. They established that equilibrium mixtures of low-molecular forms of ammonium polyphosphates $(NH_4 + H)_{n+2}P_nO_{3n+1}$ are obtained by the reaction of phosphorus(V) oxide with ammonia (or ammonium orthophosphate) in the presence of a small calculated quantity of water at comparatively low temperatures, up to 150–180°. Increase in temperature and the pressure of ammonia in the reaction vessel leads to the formation of condensed vitreous phosphates. Thus at 300–450° and an ammonia pressure of ~ 30 atm the composition of the reaction products is close to the metaphosphate composition: 16–18% NH_3 and 62–67% P_2O_5.

The authors cited confirmed that ammonium polyphosphates containing imido-groups are obtained when insufficient water vapour is present in the system. In this instance, increase in temperature leads to the production of vitreous forms of dehydrated phosphates, in which only 70–75% of the total nitrogen is present in the ammonium form, the remaining fraction being present as amido- or imido-groups.

The ammonium polyphosphates obtained by various methods are at present used not only as solid but also as liquid nitrogen-phosphorus fertilisers[36]. Dissolution of ammonium polyphosphate in water gives a liquid fertiliser with the composition 10-34-0, which is the same as that obtained by treating superphosphoric acid with ammonia. Thermal orthophosphoric acid, however, gives liquid nitrogen-phosphorus fertilisers with a lower concentration of nutrients (8-24-0).[104] According to Young[105], liquid fertilisers are obtained by dissolving ammonium polyphosphates in water or aqueous ammonia.

Since superphosphoric acid containing 76% P_2O_5 is a comparatively expensive product and is produced in insufficient quantities, it was proposed that liquid nitrogen-phosphorus fertilisers be produced from a mixture of acids: extraction phosphoric acid and a superphosphoric acid solution which had been treated with ammonia[106]. Moreover, the addition of polyphosphoric acid to orthophosphoric acid prevents the precipitation of impurities which usually separate when the latter is treated with ammonia. The introduction of potassium-containing components into the liquid nitrogen-phosphorus fertilisers makes it possible to obtain complex NPK-fertilisers with varied compositions[107,108].

Determination of the solubility of various dehydrated forms of ammonium phosphates has confirmed that it is possible to obtain ammonium polyphosphates in a form which is insoluble in water but soluble in ammonium citrate and citric acid solutions; this is of interest for the preparation of concentrated nitrogen-phosphorus fertilisers with different solubilities and mobilities in soil[109,110]. It was noted that structural factors play a part in the change in the solubility of the polyphosphates. Macromolecular crystalline polyphosphates were almost insoluble in water, whereas the amorphous compounds dissolved extensively and fairly rapidly in water. It was established that in the production of a given polyphosphate structure, a particularly important role is played by such factors as the stabilisation of various crystal lattices, the rearrangement of molecules, etc.[111] Sufficiently detailed theoretical studies of this problem have not yet been made, however, and the accumulated experimental data on the influence of various factors on the production of nitrogen-phosphorus polymeric compounds with a given solubility are not used in technology.

Practical disadvantages of most dehydrated ammonium phosphates as fertilisers are that the molar ratio of nitrogen to phosphorus does not correspond to the requirements of a large number of soils and agricultural crops, and also the hygroscopic nature of many of these salts. Many workers have therefore proposed that they be used in mixed

and liquid fertilisers. A number of proposals have been aimed at improving the physical properties by granulation and the introduction of conditioning additives.

The rapid development of sources of electrical energy, the increase in natural gas and petroleum resources, and the considerable progress in the field of high-temperature reactions, particularly electrothermal reactions, reactions in cyclones and plasma, etc., are enabling research workers to introduce new and more rational schemes for the production of highly concentrated phosphoric acid and macromolecular condensed phosphates[112,113]. In turn, the industrial development of thermal reactions for processing phosphates and preparing polymeric phosphates requires detailed physicochemical studies using the latest instrumental methods of analysis in order to elucidate the chemistry of the process and to determine the optimal conditions for carrying it out.

In conclusion, we may express the hope that the chemistry of polyphosphoric acids and dehydrated ammonium phosphates will attract the attention of a wider circle of research chemists, and that the results of their work will find varied application in various branches of the national economy, particularly in the field of concentrated and complex fertilisers.

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Three-component Complex Organometallic Catalysts

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The review deals with the literature and patent publications on the polymerisation of olefinic hydrocarbons and some of their derivatives. The mechanism of the action and the specificity of catalytic systems containing mainly ethers and amines are discussed. A small section dealing with systems based on the ether complexes of aluminium alkyls is included. The bibliography includes 236 references.

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I. INTRODUCTION

Catalytic systems based on organometallic compounds (and among them the Ziegler–Natta catalysts) have found wide application in the polymerisation of olefinic and diene hydrocarbons. Together with a high activity, these catalysts in many cases exhibit the so called stereospecificity, i.e. polymers with a definite microstructure (isotactic, syndiotactic, and *cis*- and *trans*-isomeric structures) are obtained in their presence. In order to enhance the specificity of the action of Ziegler–Natta catalysts, i.e. in order to increase the yield of structures which have the most valuable physical and mechanical properties in practice, a number of three-component catalysts have been proposed.

By introducing a third component, the molecular weight of the polymer is regulated and one attains increased rates of polymerisation and an improvement in heat exchange, the sticking of the polymer to the reactor walls, the shaft, and the blades of the stirrer is eliminated, and less dangerous components can be employed[1-9]. The third component increases the selectivity of the catalytic system in the dimerisation of α-olefins[10-12] and the cyclo-oligomerisation of dienes[13,14]. Moreover, the modified systems may prove to be the most suitable for the polymerisation of monomers containing a heteroatom in the substituent[8]. Finally, the modification of Ziegler catalysts is one of the methods helping to elucidate the details of the mechanism and nature of stereospecific polymerisation.

Certain problems associated with the effect of the modification of organometallic catalysts by various compounds[9,15-24], including nucleophilic[25-36] and electrophilic[9,29] substances and aromatic hydrocarbons[29,34,37], and also with the application of complexes of these compounds with one of the components of the catalytic system[28,38-43], have been described in the literature. Data are also available on the effect of admixtures in the catalyst, solvent, and the monomer on the polymerisation process[9,44-52]. However, the extensive experimental data accumulated hitherto have not been described systematically in the review literature and we therefore attempted to fill this gap. The present review deals with systems containing organic compounds as the third component.

2. POLYMERISATION OF α-OLEFINS

In the polymerisation of α-olefins, electron-donating compounds have found the widest application as modifying additives: ethers[1-4,53-59], esters[59-61], amines[62-66], sulphides[67,68], phosphines[69], and certain other O-, N-, S-, and P-containing compounds[70-80]. Solvents or their mixtures are frequently employed for this purpose[9,81]; particular mention should be made of the use of non-fractionated hydrocarbons as solvents[5].

The published data indicate the complex nature of the effect of additives both on the activity and the stereospecificity of the catalyst and on the molecular weight of the resulting polymers[33,35,82-85]. Investigators have frequently approached the consideration of the mechanism of the action of additives from different standpoints and contradictory views exist[25,34,39,86]. The contradictions are aggravated also by the fact that the estimation of the effect of the modification is not made under identical experimental conditions (different amounts of the additive, different order of introduction of the components, etc.).

Razuvaev and coworkers showed that, in the polymerisation of propene in the presence of the $TiCl_3-Al(C_2H_5)_3$ catalyst, the amount of additives introduced has a significant influence on the activity of the catalyst and the molecular weight of the polymer[29,37,86-88]. It has been found[87] that, for the ratio Al : Ti = 3 : 1, an increase in the ratio amine : $TiCl_3$ to 1 entails a sharp increase (by a factor of 2–3) of the molecular weight of the polymer (while the yield remains as usual). These results led the authors to the conclusion that the complexes formed prevent chain termination but do not affect the chain propagation stage. The decrease of the molecular weight of the polymer and its yield observed on increasing the amine : $TiCl_3$ ratio above the equimolar value is accounted for by the binding of the excess amine by $Al(C_2H_5)_3$. An appreciable effect of the order of introduction of the components on the experimental results was not observed. The effect of dioxan, diphenyl sulphide, and pyridine, the amounts of which were varied in the range of the ratio additive : $TiCl_3$ between zero and unity, is fully analogous to the effect of amines but in the presence of dioxan and pyridine there was an appreciable increase in the rate of the process[86].

Under these conditions, the stereospecificity of the catalyst changed insignificantly.

The addition of aromatic hydrocarbons with electron-donating properties[89] has an effect which does not differ in principle from that of other nucleophilic compounds[29,37]. Small amounts of aromatic compounds (benzene, naphthalene, anthracene, diphenyl, styrene) accelerate the polymerisation of propene, while large amounts inhibit it. The compounds can be arranged in the following series in terms of their promoting effect:

benzene ≃ toluene < ethylbenzene ~ isopropylbenzene < *o*-xylene < styrene < tetrahydronaphthalene < mesitylene < anthracene,

which agrees with their sequence in terms of decreasing ionisation potential[37].

Unsaturated aliphatic and alicyclic hydrocarbon can also serve as activators[90-94], but dienes frequently behave as effective polymerisation inhibitors[93,94]. Medvedev and coworkers[93] established that unsaturated compounds can be arranged in the following series in terms of their capacity to reduce the rate of polymerisation of ethylene:

butadiene > isoprene > styrene, isobutene > α-methylstyrene

Minsker[95] explains the effect of the modification of Ziegler–Natta catalysts by a number of polar compounds (amines, ethers, sulphides) in the following way. The reacting monomer molecules are subjected simultaneously to the action of two components of opposed types—the electron-donating ($TiCl_3$) and electron-accepting (AlR_3) components. Therefore, with increase in the amount of the additive, the rate-limiting role may pass from one stage to another (for example, from the electron-accepting to the electron-donating stage and conversely). As a result the additive can behave as a promoting agent at one concentration and as an inhibitor at another.

Vesely[96] found that tributylamine increases the molecular weight of the polymer but does not affect the rate of polymerisation of propene in the presence of the $TiCl_3$–$Al(C_2H_5)_3$ system. In this case the effect of the amine is due to its adsorption on the catalytic centres. As a result of this, the protected active centre cannot be reactivated by extraneous compounds (impurities, the solvent). A number of O-, N-, and S-containing compounds have been investigated in an analogous process[97]. It was found that, when the donor forms a stable complex with AlR_3, the decrease of the concentration of AlR_3, which is capable of giving rise to an active centre on the surface, may be inferred from the decrease of the rate of polymerisation. At a high concentration of the aluminium alkyl small amounts of electron donors increase the rate of polymerisation, while at a low concentration they decrease it. The effect of additives depends on the order of addition of the catalyst components.

Subsequently Ambrož and Hamřik[94,98] reported that electron donors capable of forming 'onium salts behave as promoting agents for catalysts with a low specific surface. For example, tributylamine increased the rate of polymerisation of propene by a factor of 2. At the same time there was an increase in the fraction of isotactic polypropylene and the yield of the amorphous fraction fell. In addition, Kodama and Atarasi[8] observed an increase of the melting point and the density of the polypropylene obtained using the $TiCl_3$–$Al(C_2H_5)_3$–ether (amine) system compared with the polymer synthesised in the presence of the two-component system. The promoting effect of the substances which they investigated varied as a function of their amount, passing through a maximum in all cases.

In order to elucidate the effect of amines in polymerisation on the $TiCl_3$–aluminium alkyl system, Milovskaya and Dolgopol'skaya[99] investigated the distribution of triethylamine between the principal components of the catalyst in the absence of the monomer. It was established that the organoaluminium compound in the complex with the amine is inactive in the polymerisation reaction. When all the components are introduced simultaneously, the amine reacts preferentially with the aluminium alkyl and not with $TiCl_3$. The authors believe that the increase of the molecular weight of the polymer in the presence of amines is due to the formation of a stable complex with the primary aluminium alkyl present in the solution and capable of displacing the polymer chain from the catalytic surface. A similar explanation of the decrease of the activity and the increase of the stereospecificity of the $TiCl_3$–$Al(C_2H_5)_3$ catalyst in the presence of $SeOCl_2$ was put forward by Soga et al.[100]

The mechanism of the action of electron-donating compounds was treated in a different way by Pirogov and Chirkov[39], who assumed that $TiCl_3$ is a fairly strong aprotic acid participating in the double composition reaction

$$TiCl_3 + AlR_3 \cdot D \rightleftarrows TiCl_3 \cdot D + AlR_3 .$$

According to the authors, three-component systems contain not less than five compounds: $TiCl_3$, AlR_3, $TiCl_3$.D, AlR_3.D, and D, their relative amounts varying during the experiment and affecting the activity and the stereospecificity of the catalyst. The activation energy for modified systems is higher than for the $TiCl_3$–AlR_3 two-component system: the values of E_{act} (in kcal mole^{-1}) are 14 for the addition of ether, 19.5 for diphenylamine, 20 for pyridine, and 23 for diethylamine, while in the absence of additives E_{act} is 11.6 kcal mole^{-1}. Thus E_{act} increases with the basicity of the donor. If both compounds are employed as complexes with a Lewis base, the systems are inactive.

The findings of Pirogov and Chirkov are confirmed by other results[28,101]. The occurrence of the reaction involving the exchange coordination of the aluminium alkyl to the donor is proved, according to Pomogailo, Matkovskii, and coworkers, by the fact that the system $VCl_4.2C_5H_5N$–$(iso\text{-}C_4H_9)_2AlCl$ is more active than $VCl_4.2C_5H_5N$–$Al(iso\text{-}C_4H_9)_3$. Since the stability of the complexes of the same ligand is determined by the strength of the Lewis acid, which for organoaluminium compounds varies in the series[102]

$$AlR_3 < R_2AlCl < RAlCl_2 < AlCl_3,$$

it follows that, in the displacement of free VCl_4 from the complex $VCl_4.2C_5H_5N$, di-isobutylaluminium chloride has proved more active than tri-isobutylaluminium.

The authors explain the greater stability of the three-component systems with respect to time compared to two-component systems by the coordination of the amine to the aluminium alkyl. The latter is also a factor which increases the molecular weight of polyethylene.

The studies by Boor[34,82,103,104] on the effect of amines on the polymerisation of propene under the influence of the Ziegler–Natta catalyst and $TiCl_3$–$Zn(C_2H_5)_2$ merits serious attention. The author attributes the fundamental role in the stereospecificity of the catalyst to the nature of the surface of the heterogeneous phase. It is suggested that the active centres are "exposed" titanium atoms and that on the $TiCl_3$ surface isolated centres of various stereospecificities exist. The latter is due to the different ways in which chlorine atoms surround the titanium atoms located in different parts of the crystal (at the corners, on the edges, and on the faces). This imparts to the centres

different capacities for coordinating α-olefin molecules. On the basis of experimental data [82,104], the effect of triethylamine on the rate of polymerisation, the isotactic properties, and the molecular weight of the polymer can be represented schematically in the following way (Fig. 1).

In the region *A* the growth of stereospecificity and the decrease of conversion are due to the binding of non-stereospecific centres, which are most exposed and accessible and also the most "acidic"; in the region *B* the constancy of the stereospecificity and the increase of the conversion are due to the increase of the activity of the remaining more stereospecific centres following the adsorption of the amine next to them (at a chlorine atom); in the region *C*, at high amine concentrations, the constancy of the stereospecificity and the decrease of conversion are caused by the deactivation of the stereospecific centres.

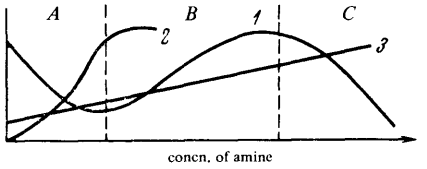


Figure 1. Variation of the degree of conversion (1), the stereospecificity of the catalyst (2), and the molecular weight of polypropylene (3) with the concentration of the amine.

Boor [34,103] divides electron-donating substances into two groups in terms of the nature of their influence. The first group combines substances which decrease the number of active centres as a result of coordination to "exposed" titanium atoms. They always increase the degree of crystallinity, the precise increase depending on the nature of the donor (Lewis bases, azulenes, aromatic compounds and olefins) and its concentration. The second group includes compounds which lower the conversion at low concentrations in consequence of the binding of the active centres and at high concentrations activate the centres (certain aliphatic and heterocyclic amines, phosphines, and azulenes). The results of thermometric titration of catalytic systems by electron donors show that, with substances of the first group, heat is not evolved while in the presence of substances of the second group the heat (exothermic) corresponds to the effectiveness of the donor as an activator of polymerisation. It must be emphasised that Boor believes that the mechanism of the activation process involves the adsorption of the amines on the surface chlorine atoms and not titanium atoms, the main role being attributed in fact to adsorption and not to coordination, since amines with large molecules (tri-n-octylamine) also activate the catalyst, i.e. the steric factor is not very important.

It has been shown in a number of studies [32,105-110] that the two-component system $TiCl_3-C_2H_5AlX_2$, which is inactive in the polymerisation of propene, becomes stereospecific following the introduction of electron-donating additives [111]. Amines, amides, ethers, 'onium salts, phosphines, and sulphides have been investigated as active additives [32,105,110]. Using *NNN'N'N"N"*-hexamethylphosphoramide (HMPA), Coover [110] showed that the rate of polymerisation of propene and the stereospecificity of the catalyst are a maximum when the HMPA: $C_2H_5AlX_2$ ratio is 0.6–0.7. Polymerisation does not occur both in the absence of HMPA and when it is present in excess of the equimolar amount. The same type of behaviour is characteristic of all strong bases, while in the case of weak bases the system is active whatever the amount of the electron donor [109].

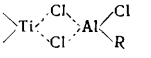
According to the literature [105,108,109,111,112], the stereospecificity of the $TiCl_3-C_2H_5AlX_2-D$ system is analogous to the stereospecificity of the $TiCl_3-(C_2H_5)_2AlX$ system. These results are due to the disproportionation (dismutation) reaction of $C_2H_5AlX_2$ in the presence of Lewis bases with formation of free $(C_2H_5)_2AlX$, which gives rise to active centres:

$$2RAlX_2 + D \rightarrow R_2AlX + AlX_3 \cdot D.$$

The occurrence of this reaction has been confirmed by cryoscopic measurements and the isolation of R_2AlX from the reaction products [108]. Ikegami et al. [113], who investigated the reaction of $(C_2H_5)_3Al_2Cl_3$ [i.e. of $(C_2H_5)_2AlCl$ and $C_2H_5AlCl_2$] with an electron donor (pyridine and dibutyl ether) and also the polymerisation of propene on $TiCl_3-(C_2H_5)_3Al_2Cl_3-D$, arrived at the same conclusion.

However, Coover [32] pointed out that the mechanism of the formation of active centres is more complex than the one discussed above and cannot be reduced solely to the reactions of the individual components. He quotes experimental data in support of this assertion [33]. Thus many compounds with high complex-forming capacity (dioxan and tetrahydrofuran) are ineffective in the polymerisation of propene when combined with $TiCl_3$ and $RAlX_2$. Infrared spectroscopy failed to reveal appreciable amounts of $(C_2H_5)_2AlCl$ in benzene solutions of $C_2H_5AlCl_2$ and HMPA.

It is believed [110] that the donor forms a complex with alkylaluminium dihalide of a type such that the active centre contains a hydrocarbon bridge. On the other hand, in the absence of a third component a dimeric structure with a halide bridge is produced:



It is noteworthy that the system β-$TiCl_3-C_2H_5AlCl_2-$HMPA is more stereospecific than the systems β-$TiCl_3-Al(C_2H_5)_3$ and β-$TiCl_3-(C_2H_5)_2AlCl$. [32,114] With increase of the stereospecificity of the catalyst, the molecular weight distribution of the polypropylene becomes narrower. In general the third component in many cases promotes a narrower molecular weight distribution [114-116].

In contrast to $TiCl_3-AlR_3-D$ systems, the activity of which increases with the basicity of the donor [$C_5H_5N > N(CH_3)_3 > N(C_2H_5)_3$], in systems with $RAlX_2$ the opposite relation is observed [32,107]: the activity of the catalytic system decreases in the series

$$N(C_4H_9)_3 > [N(CH_3)_2]_3PO \sim P(C_4H_9)_3 > (C_4H_9)_2O > (C_4H_9)_2S > C_4H_9I.$$

In a later study [98] other results were obtained for the system $TiCl_4-Al(C_2H_5)_3$, indicating the absence of a direct relation between the electron-donating properties of the additives and their effect on the polymerisation of propenes. In the presence of the system $TiCl_3-(C_2H_5)_3 \cdot Al_2Cl_3-$ether (amine), with increase of the chain length in the ether group the rate of polymerisation of propene increases, the molecular weight of the polymer rises

somewhat, and the stereospecificity of the catalyst falls[57]. The system $VCl_4-(C_2H_5)_2AlCl$ is also sensitive to the effect of the donating capacity of the Lewis base, the activity and stereospecificity of the system increasing as the strength of the Lewis base diminishes[117].

The favourable effect of Lewis bases is attributed to their capacity to increase the degree of dissociation of associated aluminium alkyls[102], which promotes the formation of active centres[107,112,118,119].

In the polymerisation of ethylene in the presence of the system $TiCl_4-LiC_4H_9$–phenetole, it was found[120] that the yield–phenetole concentration and molecular weight–phenetole concentration curves have maxima at a phenetole : Li ratio of unity. Since the above relations show a parallel variation, it was concluded that the lifetime of active centres increases while their number remains constant. An analogous observation was made for the system $VCl_4.2VP-(C_4H_9)_2AlCl-SnCl_4$ (VP = 2-vinylpyridine): the change in the rate of polymerisation and correspondingly of the molecular weight also indicates an increase of the polymerisation rate constant or the lifetime of the catalytic centre[121].

Schindler[122] established different effects of electron donors as a function of the initial ratio of the principal components of the $TiCl_4-(C_2H_5)_2AlCl-D$ catalyst. For the system with Al : Ti = 1.5, an increase of the concentration of D leads only to deactivation, while for the system with Al : Ti = 5 deactivation is observed at low donor concentration, but at high concentration the activity increases. These results are explained by invoking the existence of centres with different activities and containing Ti^{3+} and Ti^{4+}. Deactivation takes place as a result of the binding of the more acidic centres containing Ti^{4+}. According to Schindler, the increase of activity is not caused by the binding of the aluminium alkyl but by the coordination of the donor to the centre containing Ti^{3+}, as in Boor's hypotheses[103].

Table 1. Effect of the order of introduction of the components on the activity of the catalyst.

Order of addition	Monomer	Yield of polymer, g	References
$TiCl_3$—$Al(C_2H_5)_3$	propene	170*	125
$Al(C_2H_5)_3$-pyridine-$TiCl_3$	ditto	172*	125
$TiCl_3$-pyridine-$Al(C_2H_5)_3$	»	250*	125
$TiCl_4$—LiC_4H_9	ethylene	4.00	120
$TiCl_4$-phenetole-LiC_4H_9	ditto	5.25	120
LiC_4H_9—$TiCl_4$	»	1.10	120
LiC_4H_9-phenetole-$TiCl_4$	»	3.50	120
Pyridine-VCl_4-anisole-(iso-C_4H_9)$_2$AlCl	propene	0.00	117
Anisole-VCl_4-(iso-C_4H_9)$_2$AlCl-pyridine	ditto	0.9	117

*The yield is given in grammes per gramme of catalyst.

The activity of catalytic systems depends on the order of introduction of the components[117,120,123]. When anisole is added to the product of the reaction of VCl_4 and R_2AlCl, a catalyst with a lower stereospecificity is formed than following the addition of R_2AlCl to VCl_4 + anisole or of VCl_4 to R_2AlCl + anisole[117]. These results suggest that the electron donors are active components of the catalyst.

A number of workers established experimentally that it is best to introduce the catalyst components in the following sequence: the transition metal compound, the donor, and the metal alkyl (Table 1).

Having investigated the polymerisation of propene in the presence of the system $VCl_4-(C_2H_5)_2AlCl-D$, Natta et al.[124] arrived at the conclusion that the effect of anisole, the most effective of all the donors investigated (anisole, furan, isopropyl ether, diethyl ether, thiophen, pyridine, and triethylamine), is associated with its coordination both to the transition metal compound and to the organometallic compound:

$$VCl_4 + D \rightarrow VCl_4 \cdot D,$$
$$2\,(C_2H_5)_2AlCl + 2D \rightleftarrows 2\,(C_2H_5)_2AlCl \cdot D.$$

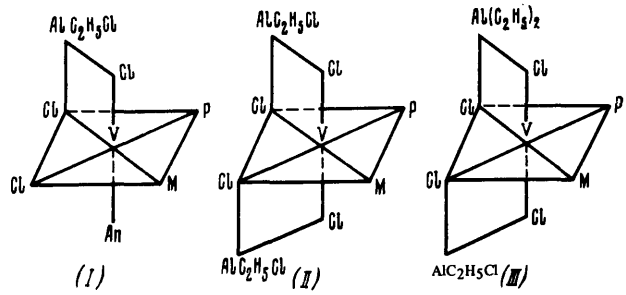


Figure 2. The structure of stereospecifically active vanadium(III) complexes in the presence (I) and absence (II and III) of anisole; P—growing molecule; M—complexed monomer; An—molecule of anisole or another Lewis base[124].

It is assumed that only free $(C_2H_5)_2AlCl$ is capable of alkylating VCl_4 or VCl_4.D. The catalytically active vanadium compound is formed by the reaction

$$(C_2H_5)_2VCl_2 \rightarrow C_2H_5VCl_2 + C_2H_5^{\cdot} \quad \text{or} \quad (C_2H_5)_2VCl_2 \cdot D \rightarrow C_2H_5VCl_2 \cdot D + C_2H_5^{\cdot}.$$

Complexes of six-coordinate V^{3+}, constituting one of the structures presented in Fig. 2, are suggested as stereospecifically active centres.

3. POLYMERISATION OF DIENE HYDROCARBONS

The polymerisation of diene hydrocarbons in the presence of Ziegler catalysts using electron-donating additives (amines, ethers, thiophen, etc.) has been described in a number of patents[126–142]. Thus it has been suggested that butadiene be polymerised at 10–50° with a $TiCl_3I-AlR_3-D$ catalyst, whereby it is possible to obtain polymers containing more than 80% of *cis*-1,4-units. The molar ratio of the catalyst components is 1 : 1.5 : 1.5.[137] As with α-olefins, the introduction of an electron donor accelerates the polymerisation[133], and regulates the molecular weight[138]. In many cases the content of the gel fraction and of cyclisation products is reduced[143]. When three-component systems are employed, the preferential formation of *cis*-1,4-,[132,139] *trans*-1,4-[138] or 1,2-structures[129,130] is achieved.

Following the introduction of ethers into the $TiI_4-Al(iso\text{-}C_4H_9)_3$ system, Dolgoplosk and coworkers[144] observed a change in the polymer microstructure: a decrease of the content of *cis*-1,4-units and hence an increase of the content of *trans*-1,4-units; the content of

1,2-units remained constant. The ethers can be arranged in the following series in terms of their effect:

dimethyl ether > ethyl methyl ether > diethyl ether > dibutyl ether,

i.e. the effect of the ether decreases with increase in the length of the hydrocarbon group and follows the decrease of the tendency towards complex formation. Therefore, in order to obtain a polymer with a high content of *cis*-1,4-units, one adds di-isopropyl ether [83,140], the electron-donating capacity of which is probably reduced owing to the steric factor. It has been noted that in the presence of electron donors the molecular weight of the polymers falls [145]. The introduction of an excess of dimethyl ether in relation to the aluminium alkyl causes a complete reversal of the microstructure with formation of a crystalline *trans*-1,4-polymer [23].

The effectiveness of sulphides as well as ethers decreases with increase in the length of the hydrocarbon group: $(C_2H_5)_2S > (C_4H_9)_2S > (C_8H_{17})_2S$. Tetrahydrofuran has a powerful effect [146]. Only compounds with a greatly reduced activity (thiophen, diphenyl sulphide, and diphenyl ether) have no influence on the chain microstructure and the polymerisation kinetics.

It is noteworthy that, when the polymerisation of isoprene is performed in diethyl ether, dioxan, aniline, dimethylaniline, and pyridine, a polymer is not formed [147]. However, in di-isopropyl ether there is a possibility of the formation of *cis*-1,4-polybutadiene [141].

The system comprising $TiCl_4$, AlI_3, and $AlHCl_2$ leads to *cis*-1,4-polybutadiene when it contains an ether or an amine in an amount equimolar with that of $AlHCl_2$. With increase of the amount of the electron donor, the content of the *trans*-units rises owing to a decrease from the content of the *cis*-units, i.e. the additives have the same effect as in the TiI_4-AlR_3 system. Analogous results were obtained in the polymerisation of isoprene under the influence of $TiCl_4-AlHCl_2.O(C_2H_5)_2$. Systems containing trimethylamine exhibit high stereospecificity [23].

The introduction of β-naphthylphenylamine into the $TiCl_4-Al(C_2H_5)_3$ system makes it possible to obtain polyisoprene not containing a gel [118]. The rate of polymerisation and the degree of conversion depend in this case on the order of introduction of the catalyst components.

The simultaneous addition of two donors (an ether and an amine) is interesting [148]. The introduction of an amine into the polymerisation system together with an ether leads in some cases to a considerable acceleration of the process. At the same time the content of the gel diminishes but the molecular weight and the polymer structure remain constant. The presence of an amine and an ether makes it possible to alter the relative amounts of the principal catalyst components without risk of increasing the content of the gel or of retarding the polymerisation.

Systems consisting of $CoCl_2$ complexes with pyridine or an alcohol in combination with R_2AlCl exhibit high stereospecificity [149-152]. It has been established that the addition of ethers, amines, and sulphides to a cobalt catalyst leads to a sharp change in the structure of the polydiene chain and a decrease of the rate of polymerisation and the molecular weight of the polymer [145]. The addition of AlR_3 has a similar influence [153-155]. The opposite effect is obtained in those cases where small amounts of water, alcohols, $AlCl_3$, $RAlCl_2$, Br_2, and other compounds are introduced [155-157]. It has been shown [154] that the complex formed from cobalt halides and $(C_2H_5)_2AlCl$ is active. There is then no oxidation-reduction interaction between the catalyst components. On the other hand, in the presence of AlR_3 cobalt is reduced to the metal with simultaneous formation of R_2AlCl and other substances. The above negative effects are associated with this reduction. In a treatment from a single standpoint of all these phenomena, Vinogradov, Dolgoplosk, and coworkers [158] start from the known fact that R_2AlCl solutions form AlR_3 under the influence of electron donors. Thus the effect of donors is analogous to that of AlR_3 additives.

On the other hand, when catalytic systems based on $CoCl_2-RAlCl_2$ [108,109,159] and $CoCl_2-AlCl_3$ [160] are employed, small amounts of donors are essential for the preparation of the *cis*-polymer, since in this case Lewis bases bind free $AlCl_3$ and suppress cationic polymerisation. Judging from the change in the degree of unsaturation of the polymer, anisole and thiophen are the most effective. Nitrogen-containing compounds (pyridine, diphenylamine, dimethylaniline) proved to be unduly powerful donors for this system; they break down the catalytic complex with formation of $CoCl_2$.

Electron-donating additives have the same influence on the homogeneous $CoCl_2.2D-(C_2H_5)_2AlCl$ system (D = pyridine or acetylacetone) [36,161] as on the heterogeneous system [145]. However, in the case of the homogeneous system the observed decrease of the molecular weight of the polymer is associated with the participation of free donors in the chain-transfer reaction [161]. This view is confirmed by the fact that an increase of the concentration of the aluminium alkyl leads to an increase of both the degree of polymerisation and the catalyst activity. An increase of the concentration of the aluminium component should lead to a decrease of the concentration of the free Lewis base. If at the same time there is an increase of the molecular weight, it follows that it is in fact the free donors which influence the chain growth limitation reaction. As already mentioned [162], the $R_2AlCl-CoCl_2.2C_5H_5N$ system is active in the preparation of the *cis*-1,4-polymer of butadiene only in the presence of water or other electron-accepting substances.

The most complete data on the kinetics of this reaction have been presented by Karchevskaya et al. [163] Water not only accelerates the polymerisation and increases the molecular weight but, after the attainment of the optimum concentration, the excess water breaks down the active centres and reduces the rate of polymerisation, but the molecular weight continues to grow. This complex effect of water is due to its dual nature, i.e. its electron-accepting and electron-donating properties.

Kinetic data for the systems $CoCl_2.2C_5H_5N-(C_2H_5)_2.AlCl-A$ (A = $AlCl_3$, $SnCl_4$, or $C_2H_5AlCl_2$) have been presented [164]. When $C_2H_5AlCl_2$ is introduced, the rate of polymerisation increases and reaches a maximum for the equimolar $(C_2H_5)_2AlCl : C_2H_5AlCl_2$ ratio. Further increase of the amount of $C_2H_5AlCl_2$ leads to the appearance of an introduction period, which is a maximum in the absence of $(C_2H_5)_2AlCl$. The molecular weight increases continuously with the amount of additive and is a maximum when the aluminium component is completely replaced by $C_2H_5AlCl_2$.

In the absence of additives, the rate of the process is low; only an oligomer was obtained: the authors suggest that the aluminium component participates in the formation of active centres and also in the decomposition of these centres and chain transfer.

Recently it has been established [165,166] that the addition to the catalytic system of halogenohydrocarbons containing two and more halogen atoms (for example CH_2Br_2 and CH_2Cl_2) increases the activity of the catalyst and makes it possible to obtain a high yield of polyisoprene containing 97-98% of *cis*-1,4-units.

4. POLYMERISATION AND COPOLYMERISATION OF OTHER MONOMERS

The effect of a large number of organic compounds containing a heteroatom on the polymerisation of styrene in the presence of $TiCl_4-Al(C_2H_5)_3$ has been investigated. It has been found that only thiophen and furan increase the stereospecificity of the system (the conversion of styrene then diminishes). Many substances (halogenobenzenes, di-n-hexyl ether, and triphenylphosphine) reduce the yield of polystyrene without affecting its structure. On the other hand, most of the compounds eliminate the stereospecificity of the catalyst, diminishing or increasing the conversion of styrene. The effect of additives reduces to binding the substances responsible for non-stereospecific cationic polymerisation. The inhibiting effect of additives is shown particularly clearly at the high concentrations employed in the study quoted above. In the polymerisation of styrene in the presence of β-$TiCl_3-Al(C_2H_5)_3$ and β-$TiCl_3-(C_2H_5)_2AlCl$ an increase of the rate of formation of the isotactic polymer is observed when straight-chain dipropyl, dibutyl, and dihexyl ethers and triethylamine are introduced up to a donor : aluminium component ratio of unity[35]. Further addition of the donor leads to a sharp decrease in the rate of polymerisation.

The effectiveness of the substances investigated decreases in the sequence

$$(n\text{-}C_6H_{13})_2O > (n\text{-}C_4H_9)_2O > (n\text{-}C_3H_7)_2O > (C_2H_5)_3N.$$

In the polymerisation of acetylene under the influence of $TiCl_4-Al(iso\text{-}C_4H_9)_3-D$, the addition of dioxan (0.05–0.1 mole per mole of $TiCl_4$) or triethylamine (0.1–0.3 mole per mole of $TiCl_4$) increases the yield of polyacetylene only when the Al : Ti ratio is less than the optimum value (for the two-component system); in other cases the additives sharply inhibit polymerisation[26].

Catalysts modified by Lewis bases are used for the polymerisation of iodo-derivatives of α-olefins in which the carbon–iodine bond is remote from the double bond[168]. The polymerisation of fluorine-containing monomers[169], symmetrical dichloroethylene[170], and vinylidene chloride[171] in the presence of similar systems has been described.

The introduction of tetrahydrofuran, triethylamine, pyridine, and diethyl ether alters sharply the activity and nature of the $Ti(OC_4H_9)_3-C_2H_5AlCl_2$ catalytic system in the copolymerisation of ethylene with vinyl chloride[172], which is evident from the change in the composition and yield of the copolymer (Table 2). On the other hand, anisole and thiophen do not have a significant influence on the activity of the system, while acetylacetone, triphenylphosphine, and dipyridyl inhibit polymerisation. According to infrared spectroscopic data, the copolymer obtained in the presence of anisole and thiophen is identical with the product synthesised without a donor and is predominantly a block copolymer. On the other hand, the spectra of the copolymers obtained in the presence of tetrahydrofuran, triethylamine, pyridine, and diethyl ether are analogous to the spectrum of the copolymer synthesised in the presence of $B(C_4H_9)_3$–t-butyl peroxide by a radical mechanism[173]. In the absence of tetrahydrofuran the composition of the copolymer is constant and the yield depends on the Al : Ti ratio.

Isotactic and syndiotactic poly(vinyl chloride) is obtained in the presence of the three component system transition metal (Ti, V, Zr, Fe, or Ni) chloride–$Al(C_2H_5)_3$–D.[174–178] In the absence of a Lewis base the polymerisation of vinyl chloride under the influence of $VOCl_3-Al(iso\text{-}C_4H_9)_3$ is slow. In the presence of ethyl acetate effective polymerisation takes place at −30°C. The authors adduce evidence for the suggested radical mechanism for this process[179].

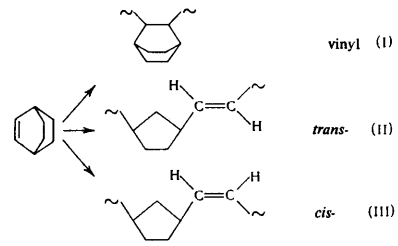
The copolymerisation of ethylene and butadiene[180–182] and ethylene and α-olefins[183–189] in the presence of three-component catalysts has been described. Under these conditions, the third component not only promotes an increased yield but also improves the physical and mechanical properties of the copolymers. The electron-donating component is then introduced as a complex with a transition metal halide[189] and more rarely with an aluminium alkyl[180].

Table 2. Copolymerisation of ethylene with vinyl chloride*.

Donor	Al:Ti	Yield, %	Vinyl chloride in copolymer, mole %	Type of copolymer	$[\eta]$**, dl g^{-1}
—	3.0	20.2	15.8	block	0.42
Tetrahydrofuran	3.0	31.6	86.8	non-regular	0.26
Triethylamine	3.0	24.0	86.1	ditto	0.24
Pyridine	3.0	22.5	89.3	»	0.30
Ether	3.0	11.1	79.5	»	0.26
Anisole	3.0	12.2	20.1	block	0.21
Thiophen	3.0	12.0	13.4	ditto	0.24
Dipyridyl	3.0	1.8	—	—	—
Acetylacetone	3.0	0	—	—	—
Triphenylphosphine	2.2	0	—	—	—

*Experimental conditions: 0.35 mole of ethylene, 0.35 mole of vinyl chloride, and 2.0×10^{-3} mole of $Ti(OC_4H_9)_3$; D : Ti = 1; 50 ml of n-heptane; temperature 50°C; duration of polymerisation 3 h.
**Measured in cyclohexanone solution at 30°C.

Lewis bases alter the mode of polymerisation of norbornene[190,191]. In the presence of the usual Ziegler catalyst norbornene is polymerised at the double bond with *trans*-ring opening, while in the presence of Lewis bases the polymerisation takes place only with *trans*- and *cis*-ring opening:



5. CATALYTIC SYSTEMS BASED ON THE ETHER COMPLEXES OF ORGANOALUMINIUM COMPOUNDS

In many studies it has been suggested that, instead of free aluminium alkyls or the addition of ethers to two-component catalysts, pre-synthesised ether complexes of aluminium alkyls be employed[1,38–42,136,142,192–202]. In some cases this leads to certain advantages; since in contrast to ether-free aluminium alkyls, the ether complexes are more convenient to prepare and handle[203] and can be obtained in the laboratory without particular difficulty[201,204–206].

Moreover, ether complexes in many cases promote the formation of polymers with valuable physical and mechanical properties. However, until recently little attention was devoted to the study of the properties of the ether complexes of organoaluminium compounds as catalysts, since it was believed[207] that ethers forming stable complexes with aluminium compounds deactivate the Ziegler–Natta systems.

The studies were mainly directed to the search for means of separating the ethers from the organometallic component. The results of the measurement of the heat of formation of triethylaluminium-ether complexes[208] suggested that the replacement of diethyl ether by an alkyl aryl ether will yield ether complexes from which ether can be readily eliminated by distillation and which can be employed as active components in catalytic systems by virtue of the presence of weakened Al ← O bonds. An inverse relation was found between the enthalpy of dissociation of the ether complexes and their polymerisation activity with respect to ethylene[41,209]. The catalyst is much less sensitive to the electron-donating capacity of the ether in the polymerisation of propene[34,202]. In this case even adducts of triethylaluminium with diethyl ether[196] and monoglyme[197] exhibit a high activity. Complexes of ethylaluminium dichloride with di-isopropyl, di-n-butyl, and di-isopentyl ethers are effective in the stereospecific polymerisation of propene[210].

It has been reported[42] that polyethylene obtained in the presence of systems with ether complexes is similar in some of its properties to the Ziegler polyethylene and, according to infrared spectroscopic data, does not contain methyl side groups[40,41].

The yield of polyethylene in the presence of the $TiCl_4$–$Al(C_2H_5)_3.C_6H_5OC_2H_5$ catalyst[202] depends on the Al : Ti ratio, but this dependence is not as pronounced as for the ether-free catalyst[211]. It is well known that the activity of the catalyst is higher when it is formed in the presence of the monomer. A similar effect is shown also for ether complexes[202]. In the presence of ether or the monomer, the molecules of which behave as ligands, the following complexes may be formed:

$$[TiCl_3]^+ \xrightarrow{ROR'} [TiCl_3]\ (I) \quad \text{or} \quad [TiCl_3]^+\ (II)$$

(I): $^{+}O(R)R'$; (II): $CH_2{=}CH_2$

As a result, further reaction between the components of the bimetallic complex $[TiCl_3]^+[Al(C_2H_5)_3Cl]^-$ is hindered, which leads to its deactivation. Then the Ti–C bond in compound (II) should be comparable in strength to the Ti ← O bond in compound (I). For ethylene, this is observed in the case of ethers containing an aryl group (weak nucleophilic agents). Depending on the monomer, different ethers cause deactivation.

Mardykin et al.[212] compared the effectiveness of ether complex systems with ether-free systems in the polymerisation of styrene. The corresponding results are presented in Table 3, from which it follows that the $TiCl_n$–$Al(C_2H_5)_3$.ether systems are active in the stereospecific polymerisation of styrene.

With the aid of the ether complexes of aluminium alkyls optically active poly-α-olefins have been obtained even from optically inactive olefins[217–219].

The ether complexes of aluminium alkyls are also active in the polymerisation of dienes (isoprene, butadiene, etc.), the ether complexes of tri-isobutylaluminium being most often used in such cases. In the presence of systems of this kind polyisoprene with the properties of natural rubber is obtained[142,198–200,220].

The polymerisation of penta-1,3-diene[219], hexa-1,3,5-triene[221], and other conjugated trienes[222] in the presence of ether complexes has been described.

Together with the ether complexes of aluminium alkyls, complexes of organoaluminium compounds with amines have been employed in the polymerisation of olefins[223] and organic sulphide complexes of aluminium alkyls have been employed in the polymerisation of dienes[224].

Table 3. Stereospecificity of the $TiCl_n$–AlR_3 (a) and $TiCl_n$–AlR_3.ether (b) systems in the polymerisation of styrene.

Conversion	Duration of polymerisation, h	Crystallinity, %	Yield of crystalline polymer, %	System	References
		Catalysts with $TiCl_4$			
9	2–6	89	8.0	a	213
5–28	3–4	44–81	0.6–15.6	a	214
13	4	38.8*	4.9	a	167
3	7	50	1.7	a	215
13–100	2–5	1–20	0.9–3.8	b	212
		Catalysts with $TiCl_3$			
71	6.5	94	66.7	a	216
16–66	3–12	85–90	13.3–60	b	212

*Extraction with ethyl methyl ketone and in the remaining cases with acetone.

The copolymerisation of ethylene with nitrogen-containing monomers (acrylonitrile, diallylamine, etc.) previously bound in complexes with one of the components of the Ziegler catalyst is of considerable interest[225,226].

The above review of the applications of three-component systems shows that a positive effect is achieved by introducing into the Ziegler–Natta catalysts substances of different types: ethers, amines, phosphorus derivatives, sulphur derivatives, alcohols, water, salts, etc. Evidently the mechanism of the action of such a wide variety of reagents cannot be common to all of them. Moreover, the role of the third component must be considered in relation to a definite class of substances constituting the basis of the catalytic system. Until recently in the study of three-component systems the principal role was attributed to processes involving the chemisorption of electron-donating compounds on the active centres of the catalyst[29,82]. Admittedly, in most cases the third component was introduced to a complex already formed from the principal components (MX_n–ER_m; M = transition metal, X = halogen, and E = Al, Mg, Li, etc.). In these cases the effect of the donor is shown by virtue of its binding in a complex (or chemisorption on) already existing polymerisation centres.

The third component has a more profound specific effect when it interacts with one of the principal components of the catalyst before the formation of the catalytic complex proper. The complexes of the catalyst components formed under these conditions will behave differently in the chemical reaction and will yield products (some of which are active centres) differing from those obtained when free (non-complexed) components are employed.

Thus, together with chemisorption, in three-component systems account must be taken also of chemical reactions between all three components. One of the principal reactions in the formation of the catalytic complex is the alkylation and reduction of the transition metal compound:

$$AlR_3 + TiCl_4 \rightarrow RTiCl_3 + R_2AlCl;\ RTiCl_3 \rightarrow TiCl_3 + 1/2\,R_{(+H)} + 1/2\,R_{(-H)}.$$

Nucleophilic compounds accelerate this reaction [25,31,38,158]. If the Ti–C bond is assumed to be the active centre [227-231], the increase of the rate of alkylation of titanium will lead to an increase in the number of active centres and a corresponding acceleration of the polymerisation process. The electron donor coordinated to the catalytic complex losens the Ti–C bond by virtue of the increase of the electron density around the titanium atom and thereby facilitates the insertion of the monomer into the active centre [232]. Moreover, as the reaction between the components of the catalytic system proceeds, there is a possibility of the formation of new complexes, since certain reaction products are stronger Lewis bases. For example, in the $TiCl_4-AlR_3$ system these are R_2AlCl, $RAlCl_2$, and $AlCl_3$. As a result, the donor is transferred to the powerful new electron acceptors appearing in the system and new more stable complexes are formed: $R_2AlCl.D$, $RAlCl_2.D$, and $AlCl_3.D$. In turn, these complexes behave differently than the corresponding free compounds. Thus, under certain conditions, the complexes $R_2AlCl.D$ and $RAlCl_2.D$ disproportionate with formation of an additional amount of the initial organometallic component:

$$2R_2AlCl + D \rightarrow AlR_3 + RAlCl_2 \cdot D,$$
$$2RAlCl_2 + D \rightarrow R_2AlCl + AlCl_3 \cdot D \text{ etc.}$$

Consequently in the presence of the donor, the effective concentration of the organometallic component increases which, depending on its initial concentration, determines the effectiveness of the catalytic system. However, not all donors are capable of being transferred from one component to another. Some of these are irreversibly bound in complexes with the initial components and are cleaved:

$$RAlX_2 + R'OR'' \rightarrow RAlX_2 \cdot O\begin{matrix}R'\\R''\end{matrix} \rightarrow RAlX(OR') + R''X,$$

$$TiCl_4 + R'OR'' \rightarrow TiCl_4 \cdot O\begin{matrix}R'\\R''\end{matrix} \rightarrow TiCl_3OR' + R''Cl.$$

In the presence of $AlCl_3$ and other Lewis acids alkyl aryl ethers readily rearrange to alkylphenols [233]. Phenol and its alkyl derivatives have been detected [234] among the products of the reaction between $TiCl_4$ and $Al(C_3H_7)_3$. $.C_6H_5OCH_3$.

Electron donors reacting in the above manner deactivate (disrupt) the catalyst when present in equimolar amounts in relation to the main components. Only those donors which are not cleaved or are cleaved only to a slight extent exhibit a positive modification effect when present in large amounts.

In the latter case the degree of reduction of the transition metal and hence the activity of the catalytic system increase owing to the formation of alkoxy-derivatives, since the presence of RO groups in the $TiCl_4-(C_2H_5)_2AlCl$ system in amounts up to 25% greatly increases the degree of reduction of $TiCl_4$. [235] Systems containing alkoxy-derivatives of titanium proved to be more effective. The effect of small amounts of active substances such as alcohols and water should be treated similarly.

The complexity of the relation between the molecular weight of the polymer and the amount of the donor is due to the fact that the donor can (1) behave as a chain-transfer agent, (2) can form complexes with chain-transfer agents, (3) can alter the chain propagation rate constant or the lifetime of the active centre by forming complexes with the latter, and (4) can influence the molecular weight by altering the relative amounts and the activities of the main components.

The differences in the electron-donating capacity and the structure of additives are shown in the fact that they exhibit the same effect at unequal concentrations [236]. As a rule, small amounts of the donor increase and large amounts reduce the molecular weight of the polymer.

The stereospecificity of catalytic systems depends similarly on the content of the electron-donating compound. When a third component is introduced, the number and activity of the stereospecific and non-stereospecific centres change owing to both chemical reactions and adsorption processes.

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Redox Reactions of Atoms and Radicals with Ions in Solution

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The reactions of hydrogen atoms and various radicals ($HO^{\cdot}$, $HO_2^{\cdot}$, $RO_2^{\cdot}$, $RO^{\cdot}$, $R^{\cdot}$, diphenylpicrylhydrazyl) in solution with cations and complexes of metals of variable valency and also with anions are surveyed, and their mechanism is discussed. The rate constants of these reactions are tabulated. A list of 130 references is included.

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1. INTRODUCTION

For a long time research workers studying the changes undergone by free radicals concentrated their attention on reactions with molecules which involve substitution and addition. The reactions of radicals with metal ions—electron-transfer reactions—became a subject for quantitative investigation only in the 1960s. Whereas about 20 papers were published on this topic before 1960, the number of publications which appeared during the 1960s exceeded 100.

The enhanced interest taken by investigators in the reactions of free radicals with ions is due to the active part played by these processes in various chain and free-radical chemical reactions. Redox reactions of hydrogen atoms and hydroxy-radicals with various ions take place in photochemical and radiation-chemical systems[1]. The decomposition of hydrogen peroxide involves the formation of hydroxyl and hydroperoxy-radicals, which react with metal ions[2]. The introduction of ions of metals having variable valency into a system in which radical polymerisation is taking place leads to chain termination as a result of reactions between the metal ions and polymer macroradicals[3]. Reactions between peroxy-radicals and compounds of metals with variable valency play an important part in the catalytic liquid-phase oxidation of hydrocarbons[4]. Reactions between alkyl radicals and salts of heavy metals form the basis of various organic syntheses.

A free radical possesses an unpaired electron, and is able to oxidise a reducing ion by removing an electron from the latter, e.g. $Fe^{2+} + HO\cdot \rightarrow Fe^{3+} + HO^-$, but it is able also to reduce an oxidising ion, by donating its electron to the latter, e.g. $Fe^{3+} + H\cdot \rightarrow Fe^{2+} + H^+$.

The redox reactions of free radicals with ions are often very rapid. For example, the polyacrylamide radical reacts with ferric ions with a rate constant of the order of 10^3 M^{-1} s^{-1}; the hydrogen atom and hydroxyl and hydroperoxy-radicals react in water with ions of metals having variable valency with rate constants of the order of 10^8-10^{10} M^{-1} s^{-1}. The reactions of atoms and radicals with ions of metals having variable valency may have various mechanisms: in one case the radical replaces the solvent molecule in the inner coordination shell of the ion; in another case electron transfer takes place from the ion through the medium to the radical or conversely; and in a third case reaction of the radical with a ligand is followed by rearrangement of the electronic structure of the complex.

The reactions of atoms and radicals with ions and complexes are studied quantitatively by methods developed to measure the rate constants of rapid reactions[5]—flow methods (FM), the flash method (FP), pulse radiolysis (PR), and the inhibiting effect of a reactant on the chain reaction—but the most widely used is the method of competing reactions (MCR), which enables the ratio of the rate constants of two parallel reactions involving the same species (e.g. the hydrogen atom) to be determined from the composition of the products.

2. REACTIONS OF HYDROGEN ATOMS

The hydrogen atom is an active reducing agent, which reacts rapidly with oxidising ions:

$$H^{\cdot} + M^{n+1} \rightarrow H^+ + M^{n+}.$$

Such a reaction occurs either by addition of the hydrogen atom to one of the ligands with rearrangement of the electronic structure of the complex, e.g.

$$FeOH^{2+} + H^{\cdot} \rightarrow FeH_2O^{2+},$$
$$MnO_4^- + H^{\cdot} \rightarrow HMnO_4^- \rightleftharpoons H^+ + MnO_4^-,$$

or as a result of the transfer of an electron from the hydrogen atom to the central atom of the complex.

The rate constant for reaction of hydrogen atoms with ions of metals having variable valency is almost independent of the redox potential of the ion. For the ions Cu^{2+}, $Fe(CN)_6^{3-}$, Fe^{3+}, and Ag^+, for example, the redox potential and $\lg k(H\cdot + \text{ion})$ are respectively 0.15 and 7.77 (Cu^{2+}), 0.36 and 9.60 $[Fe(CN)_6]^{3-}$, 0.77 and 7.34 (Fe^{3+}), and 0.8 and 10 (Ag^+). The hydrogen atom reacts with MnO_4^- and Ag^+ with diffusion-controlled rate constants of the order of 10^{10} M^{-1} s^{-1}.

The hydrogen atom behaves as an oxidant on reaction with reducing ions. For example, hydrogen atoms oxidise I^- to I·, Fe^{2+} to Fe^{3+}, etc. The following mechanism has been suggested[6] for the oxidation of Fe^{2+} ions by hydrogen atoms:

$$H^{\cdot} + Fe^{2+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} FeH^{2+}; \quad FeH^{2+} + H^+ \xrightarrow{k_2} Fe^{3+} + H_2.$$

Approximate values of the rate constants[6] are $k_1 \simeq 10^9$ and $k_{-1}/k_2 \simeq 0.02$. A different mechanism has been proposed[7] for the reaction of hydrogen atoms with I^-, according to which the hydrogen atom adds to a hydrogen ion with the formation of H^+_{2aq}, and this species oxidises the iodide ion:

$$H^\cdot + H^+_{aq} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H^+_{2aq} \quad H^+_{2aq} + I^- \xrightarrow{k_2} H_2 + I^\cdot$$

where $k_1 \simeq 10^2 - 10^3$ M^{-1} s^{-1}.

Table 1 lists rate constants for the redox reactions of hydrogen atoms with various cations and anions. Where the method of competing reactions has been used, the competing compound is indicated. The hydrogen atoms were obtained radiochemically using an aqueous solution or by passing an electric discharge through hydrogen and then bubbling the H_2 + H· through an aqueous solution.

Table 1. Reactions of hydrogen atoms with ions in aqueous solution at room temperature (20–25°C).

Ion	Conditions	lgκ	Method	Ref.
$Cr(NH_3)_5Cl^{2+}$	pH=5	6.255	MCR, $(CH_3)_2CDOH$	8
$CrCl_2(H_2O)^+_4$	pH=5	7.30	MCR, $(CH_3)_2CDOH$	8
Mn^{2+}	pH=6	7.40	MCR, $(CH_3)_2CDOH$	8
Fe^{2+}	pH=0.4 (H_2SO_4)	7.20	MCR, O_2	9
Fe^{2+}	pH=2.1 (H_2SO_4)	7.115	MCR, O_2	9
Fe^{2+}	pH=2.1 (H_2SO_4)	7.13	MCR,	10
Fe^{2+}	0.4 *M* H_2SO_4	7.30	PR	11
Fe^{3+}	0.4 *M* HCl	7.90	MCR, O_2	12
Fe^{3+}	pH=0.4	6.08	MCR, O_2	9
Fe^{3+}	pH=1.57	7.34	MCR, O_2	9
Fe^{3+}	pH=2.1	7.98	MCR, O_2	9
Fe^{3+}	0.01 *N* H_2SO_4	7.98	MCR, D_2	10
Fe^{3+}	0.4 *M* H_2SO_4	6.20	MCR, Fe^{2+}	13
Fe^{3+}	pH=2 (H_2SO_4)	7.955	PR	14
$FeOH^{2+}$	pH=0.7÷2.7	8.88	MCR, CH_3OH	15
$FeCl^{2+}$	pH=0.1	9.655	MCR, O_2	12
$FeCl^+_2$	pH=0.1	9.955	MCR, O_2	12
$Fe(CN)^{3-}_6$	pH=1÷3	9.60	MCR, $HCOO^-$	16
$Fe(CN)^{3-}_6$	pH=7	9.60	MCR, $(CH_3)_2CHOH$	17
$Fe(CN)^{3-}_6$	pH=7	9.48	MCR, C_2H_5OH	18
$Fe(CN)^{3-}_6$	pH=1.1	9.68	MCR, C_2H_5OH	18
$Fe(CN)^{3-}_6$	acid	9.56	MCR, $(CH_3)_2CHOH$	19
$Co(NH_3)^{3+}_6$	pH=4÷6	6.27	MCR, H·	20
$Co(NH_3)^{3+}_6$	pH=4–6	6.20	MCR, CD_3OH	21
$Co(NH_3)_5H_2O^{3+}$	pH=4–6	5.65	MCR, H	20
$Co(NH_3)_5OH^{2+}$	pH=4–6	7.40	MCR, $(CH_3)_2CDOH$	21
$Co(NH_3)_5OH^{2+}$	pH=4÷6	7.49	MCR, H	20
$Co(NH_3)_5F^{2+}$	pH=4÷6	6.08	MCR, CD_3OH	21
$Co(NH_3)_5F^{2+}$	pH=4÷6	6.04	MCR, H·	20
$Co(NH_3)_5F^{2+}$	0,1 *M* $HClO_4$	⩽6.30	MCR, C_2H_5OH	22
$Co(NH_3)_5Cl^{2+}$	pH=4÷6	7.86	MCR, H·	20
$Co(NH_3)_5Cl^{2+}$	pH=4–6	8.34	MCR, $(CH_3)_2CDOH$	21
$Co(NH_3)_5Cl^{2+}$	pH=1	9.20	MCR, C_2H_5OH	22
$Co(NH_3)_5Br^{2+}$	pH=4÷6	8.66	MCR, H·	20
$Co(NH_3)_5Br^{2+}$	pH=1	10.15	MCR, C_2H_5OH	22
$Co(NH_3)_5Br^{2+}$	pH=4–6	9.00	MCR, $(CH_3)_2CDOH$	21
$Co(NH_3)_5I^{2+}$	pH=4–6	9.48	MCR, $(CH_3)_2CDOH$	21
$Co(NH_3)_5I^{2+}$	pH=4÷6	9.52	MCR, H·	20
$Co(NH_3)I^{2+}$	pH=1!	10.52	MCR, C_2H_5OH	22
$Co(NH_3)_5CN^{2+}$	pH=4–6	7.57	MCR, $(CH_3)_2CDOH$	21
$Co(NH_3)_5CN^{2+}$	pH=1	7.785	MCR, C_2H_5OH	22
$Co(NH_3)_5CNS^{2+}$	pH=1	9.80	MCR, C_2H_5OH	22
$Co(NH_3)_5N^{2+}_3$	pH=4–6	8.59	MCR, $(CH_3)_2CDOH$	21
$Co(NH_3)_5N^{2+}_3$	pH=1	9.04	MCR, C_2H_5OH	22
$Co(NH_3)_5NO^{2+}_2$	pH=1	8.20	MCR, C_2H_5OH	22
$Co(NH_3)_5(NO_3)_3$	pH=1	8.98	MCR, C_2H_5OH	22
$Co(NH_3)_6PO_4$	pH=1	⩽5.83	MCR, C_2H_5OH	22
$Co(NH_3)_5OCOCH^{2+}_3$	pH=1	⩽6.11	MCR, C_2H_5OH	22
$Co(NH_3)_5OCOCF^{2+}_3$	pH=1	⩽5.43	MCR, C_2H_5OH	22
$Co(NH_3)_5$ fumarate $-H^{2+}$	pH=1	9.785	MCR, C_2H_5OH	22
$Co(CN)^{3-}_6$	pH=1	7.30	MCR, C_2H_5OH	

Table 1 (cont'd.).

Ion	Conditions	lgκ	Method	
$Co(CN)^{3-}_6$	pH=5	8.955	MCR, $(CH_3)_2CDOH$	8
$Co(en)_3Cl^{2+}_2$	pH=5	8.84	MCR, $(CH_3)_2CDOH$	8
$Co(en)_3CO^+_3$	pH=5	<6.30	MCR, $(CH_3)_2CDOH$	8
Ni^{2+}	pH=7	<5.0	MCR, C_2H_5OH	18
Cu^{2+}		7.77	PR	8
Cu^{2+}	pH=7	8.70	MCR, $(CH_3)_2CDOH$	8
Cu^{2+}	pH=1	7.76	MCR, HCO_2H	23
Cu^{2+}	pH=1	8.18	MCR, CH_3COCH_3	24
Cu^{2+}	pH=7	8.78	MCR, $(CH_3)_2CHOH$	17
Cu^{2+}	pH=0.7÷2.7	7.78	MCR, CH_3OH	15
Zn^{2+}	pH=7	<5.0	MCR, C_2H_5OH	18
As^{3+}	pH=2.7	~9.00	MCR, H_2O_2	25
Ag^+	pH=7	10.04	PR	26
Ag^+	pH=7	9.60	MCR, C_2H_5OH	18
Cd^{2+}	pH=7	<5.0	MCR, C_2H_5OH	18
Sn^{2+}	pH=1	10.90	MCR, Fe^{3+}	27
Sn^{4+}	pH=1	6.40	MCR, Fe^{3+}	27
SnF^-_3	pH=5	9.30	MCR, $(CH_3)_2CDOH$	8
SnF^{2-}_6	pH=5	6.955	MCR, $(CH_3)_2CDOH$	8
Hg^{2+}	pH=7	10.40	MCR, $(CH_3)_2CDOH$	18
Tl^{1+}	pH=1,5	8.00	MCR, $(CH_3)_2CDOH$	8
OH^-	pH=11÷13	7.36	MCR, CH_3COCH_3	24
OH^-		7.30	PR	8
OH^-	pH=7.5÷12.5	7.08	MCR, $ClCH_2CO^-_2$	28
OH^-	pH=11.5	~7.30	PR	29
CN^-	pH=7	9.415	MCR, $(CH_3)_2CDOH$	8
CNS^-	pH=7	8.23	MCR, $(CH_3)_2CDOH$	8
HCO^-_3	pH=7	~4.48	MCR, CH_3OH	24
NO^-_2	pH=7	8.78	MCR, CH_3OH	30
NO^-_3	pH=7	8.12	MCR, $(CH_3)_2CHOH$	17
NO^-_3	pH=6	8.78	MCR, $(CH_3)_2CHOH$	8
NO^-_2	pH=7	9.00	MCR, CH_3OH	18
NO^-_2	pH=8	9.38	MCR, C_2H_5OH	22
NO^-_2	pH=6	8.955	MCR, $(CH_3)_2CDOH$	8
NO^-_3	pH=11–13	6.845	MCR, CH_3COO^-	24
NO^-_3	pH=7	7.38	MCR, $(CH_3)_2CHOH$	17
NO^-_3	pH=1.1	7.08	PR	20
NO^-_3	pH=10–13	6.58	PR	20
NO^-_3	pH=7	6.845	MCR, C_2H_5OH	18
NO^-_3	acid	7.36	MCR, $(CH_3)_2CHOH$	19
F^-	pH=8.5	4.175	MCR, CD_3OH	31
CrO^{2-}_4	pH=7	10.00	MCR, C_2H_5OH	18
$Cr_2O^{2-}_7$	pH=7	10.20	MCR, C_2H_5OH	18
MnO^-_4	pH=3	10.45	PR	32
MnO^-_4	pH=3	10.39	PR	33
MnO^-_4		10.27	PR	26
MnO^-_4		10.28	PR	34
BrO^-_3	pH=7	7.30	MCR, $(CH_3)_2CHOH$	8
IO^-_3	pH=7	7.77	MCR, $(CH_3)_2CHOH$	8
I^-_2	pH=3.5÷11	7.255	FP	35

3. OXIDATION OF IONS BY FREE HYDROXYL

The hydroxy-radical is a very active oxidant, rapidly oxidising not only cations of metals of variable valency (Fe^{2+}, Ce^{3+}, Tl^+) but also anions such as HCO^-_3, HSO^-_4, and NO^-_2.

The rate constant for oxidation of the Fe^{2+} ion by hydroxyl is 3×10^8 M^{-1} s^{-1}, which exceeds the rate of substitution of the water molecules in the inner coordination sphere of the $Fe(H_2O)^{2+}_6$ ion by factors of 10^2-10^3. Hence the oxidation of Fe^{2+}_{aq} does not involve entry of the hydroxyl into its inner coordination sphere. Two alternative mechanisms can be suggested for this process—electron transfer from Fe^{2+}_{aq} to HO· through the solvent or

abstraction by hydroxyl of a hydrogen atom from a water molecule in the inner coordination sphere of Fe^{2+}_{aq}:

$$HO^{\cdot} + Fe(H_2O)_6^{2+} \rightarrow H_2O + Fe(H_2O)_5OH^{2+}.$$

The $Fe(CN)_6^{4-}$ ion is oxidised by hydroxyl with a diffusion rate constant of $\sim 10^{10}$ M^{-1} s^{-1}; oxidation probably occurs by transfer of an electron from the complex ion to hydroxyl. The Cu^{2+} ion is oxidised by hydroxyl to tervalent copper.

The rate constant of the reaction between hydroxyl and the chloride ion depends on pH:

pH	0	1	2	3
lg$k$	9.60	8.60	7.60	7.20
$k/[H^+]$	$4\cdot10^9$	$4\cdot10^9$	$4\cdot10^9$	$1.6\cdot10^{10}$.

A possible explanation is that oxidation of Cl^- is accomplished by the reaction

$$HO^{\cdot} + HCl \rightarrow H_2O + Cl^{\cdot}.$$

Table 2. Reactions of hydroxyl radical with ions in aqueous solution at room temperature.

Ion	Conditions	lgκ	Method	Ref.
Cr^{3+}	acid	8.49	MCR, H_2	36
Mn^{2+}	pH=7	>8.15	PR	37
Fe^{2+}	pH=1	8.48	MCR, H_2	38
Fe^{2+}	pH=1	8.505	MCR, H_2	39
Fe^{2+}	pH=1.6	8.505	MCR, H_2	9
Fe^{2+}	pH=2.1	8.40	MCR, H_2	9
Fe^{2+}	pH=2	8.415	PR	40
Fe^{2+}	pH=0.4	8.43	PR	41
Fe^{2+}		8.54	MCR	42
$Fe(CN)_6^{4-}$	pH=2.5÷10.5	9.32	MCR, HCO_2^-	43
$Fe(CN)_6^{4-}$	pH=7	10.23	PR	44
$Fe(CN)_6^{4-}$	pH=10.7	9.915	MCR, C_2H_5OH	45
$Fe(CN)_6^{4-}$	pH=9	9.875	MCR, $NOC_6H_4N(CH_3)_2$	46
$Fe(CN)_6^{4-}$	pH=3—10	10.03	PR	47
Cu^{2+}	pH=7	8.545	PR	48
Sn^{2+}	pH=1	9.30	MCR, Fe^{2+}	27
Tl^{1+}	pH=7	9.88	PR	49
Tl^{1+}	pH=1	9.95	MCR, Ce^{3+}	50
Ce^{3+}		8.34	MCR	51
Ce^{3+}		8.54	MCR, H_2	8
Ce^{3+}	pH=1	8.34	MCR, HCO_2H	50
OH^-		8.555	FP	52
NO_2^-	pH=7	9.60	MCR	8
NO_2^-	pH=7	9.40	MCR, H_2O_2	53
NO_2^-	pH=7	9.555	MCR, CO_3^{2-}	54
NO_2^-	pH=7	9.40	PR	55
NO_2^-	pH=7	9.38	MCR, NO	56
NO_2^-	pH=9	9.69	MCR, $NOC_6H_4N(CH_3)_2$	46
NO_3^-	pH=9	<5.7	MCR	8
N_3^-	pH=9	9.81	MCR, $NOC_6H_4N(CH_3)_2$	46
CN^-	pH=9	9.43	MCR, $NOC_6H_4N(CH_3)_2$	46
PO_3^{3-}	pH=10.7	9.28	MCR, CO_3^{2-}	54
$H_2PO_2^-$	pH=10.7	8.97	MCR, CO_3^{2-}	54
$H_2PO_2^-$	pH=7	<7.0	MCR, I^-	57
SO_3^{2-}	pH=7	9.08	MCR, CO_3^{2-}	55
HSO_3^-	pH=7	9.32	MCR, CO_3^{2-}	55
H_2SO_4	pH=1	5.60	MCR	58
HSO_4^-	pH=1	7.52	MCR, HCO_2H	27
HSO_4^-		5.30	MCR, H_2	59
HSO_4^-		5.70	MCR, H_2	36
HSO_4^-		7.30	FP	59
CNS^-	pH=7	9.82	PR	54
CNS^-	pH=7	9.115	PR	55
CNS^-	pH=13.5	9.00	PR	60
CNS^-	pH=2	9.76	MCR, thymine	61
Cl^-	pH=0	9.60	MCR, thymine	62

Table 2 (cont'd.).

Ion	Conditions	lgκ	Method	Ref.
Cl^-	pH=1	8.60	MCR, thymine	62
Cl^-	pH=2	7.60	MCR, thymine	62
Cl^-	pH=4	6.60	MCR, thymine	62
Cl^-	pH=3	7.20	MCR	63
Cl^-	pH=9	5.85	MCR, $NOC_6H_4N(CH_3)_2$	46
Cl^-	pH=0	9.60	MCR, OH	64
Cl^-	pH=0	9.60	PR	65
Cl^-	pH=3	7.30	PR	65
AsO_2^-	pH=10.7	9.66	MCR, CO_3^{2-}	54
AsO_2^-	pH=9	9.66	MCR, $NOC_6H_4N(CH_3)_2$	46
SeO_3^{2-}	pH=7	9.43	PR	54
Br^-	pH=0	10.20	MCR, OH	64
Br^-	pH=0—2	10.555	MCR, H_2	66
Br^-	pH=7	8.115	MCR, C_2H_5OH	67
Br^-	pH=2	9.70	PR	68
Br^-	pH=3	9.34	MCR	63
Br^-	pH=7	9.00	PR	68
Br^-	pH=5—9	9.08	PR	69
Br^-	pH=7	9.20	MCR, NO	70
Br^-	pH=7	9.13	MCR, H_2O_2	71
Br^-	pH=7	8.115	PR	55
Br^-	pH=10.5	8.89	MCR, $C_6H_5CO_2^-$	45
Br^-	pH=1.3	9.765	MCR, C_2H_5OH	72
Br^-	pH=9	8.83	MCR, $OC_6H_4(CH_3)_2$	73
I^-	pH=7	9.20	FP	52
I^-	pH=7	9.845	PR	32
I^-	pH=3	9.52	MCR	63
I^-	pH=7	10.01	PR	44
I^-	pH=10.5	9.96	MCR, $C_6H_5CO_2^-$	45
I^-	pH=9	9.935	MCR, $NOC_6H_4N(CH_3)_2$	46
CO_3^{2-}	pH=7	7.90	PR	55
CO_3^{2-}	pH=10.7	8.30	MCR, CNS^-	54
CO_3^{2-}	pH=11.6	8.62	PR	74
CO_3^{2-}	pH=13	7.64		8
CO_3^{2-}	H_2O, pH=11	8.48	PR	44
CO_3^{2-}	H_2O, pH=10.5	8.48	MCR, $C_6H_5CO_2^-$	45
HCO_3^-	H_2O, pH=7	7.00	PR	75
$C_2O_4^{2-}$	H_2O, pH=9	7.70	MCR, $NOC_6H_4N(CH_3)_2$	46
$C_2O_4^{2-}$	H_2O	6.78	MCR, C_2H_5OH	72
$C_2O_4H^-$	H_2O	7.545	MCR, C_2H_5OH	72
$C_2O_4H_2$	H_2O	7.0	MCR, C_2H_5OH	72

A somewhat analogous reaction takes place in the oxidation of bromide ions, since here, too, k increases with the hydrogen-ion concentration:

pH	0	2	3	7
lg$k$	10.20	9.70	9.34	9.00 .

Oxidation of the iodide ion by hydroxyl is independent of pH:

$$I^- + HO^{\cdot} \rightarrow I^{\cdot} + HO^-.$$

Table 2 gives rate constants for the oxidation of ions by hydroxyl radicals, which were obtained photochemically and radiation-chemically. In most cases the method of competing reactions was used to measure the rate constants.

Measured rate constants quoted in different papers usually show good agreement. The mean logarithms of the rate constants are

$$\lg k\,(Fe^{2+} + HO^{\cdot}) = 8.47 \pm 0.04,\ \lg k\,(Fe(CN)_6^{4-} + HO^{\cdot}) = 9.85 \pm 0.28,$$

$$\lg k\,(Ce^{3+} + HO^{\cdot}) = 8.40 \pm 0.09,\ \lg k\,(I^- + HO^{\cdot}) = 9.75 \pm 0.25,\ \lg k\,(CO_3^{2-} + HO^{\cdot}) = 8.30 \pm 0.$$

The rate constant of the reaction ·OH + Ion is independent of the free energy of reaction:

Ion	Br^-	Ce^{3+}	Mn^{2+}	I^-	Fe^{2+}	$Fe(CN)_6^{4-}$
ΔG, kcal mole^{-1}	−3	−8	−10	−18	−26	−36
lg$k$	9.0	8.4	8.1	9.5	8.5	9.9 .

4. REACTIONS OF ALKYL AND ARYL RADICALS WITH SALTS OF METALS HAVING VARIABLE VALENCY

Reaction of the Type $R\cdot + MX_n \rightarrow RX + MX_{n-1}$

The Sandmeyer reaction—decomposition of ArN_2X under the influence of CuX—involves the intermediate formation of an aryl radical. This is evident if only from the formation of the aryl iodide by the reaction[76]

$$Ar\cdot + I_2 \rightarrow ArI + I\cdot$$

when the arenediazonium chloride is decomposed by copper(I) chloride in the presence of molecular iodine. Kochi proposed the following mechanism for this reaction[76]

$$ArN_2^+ + CuCl_2^- \rightleftharpoons ArN_2CuCl_2 ,$$
$$ArN_2CuCl_2 \rightarrow Ar\cdot + CuCl_2 + N_2 ,$$
$$Ar\cdot + CuCl_2 \rightarrow ArCl + CuCl .$$

The last stage involves oxidation of the aryl radical by copper(II) chloride occurring as a radical substitution.

A similar primary step occurs in the Meyerwein reaction, whose mechanism can be represented[76,77]

$$ArN_2^+ + CuCl_2^- \rightleftharpoons ArN_2CuCl_2 \rightarrow Ar\cdot + N_2 + CuCl_2 ,$$
$$Ar\cdot + CH_2{=}CHY \rightarrow ArCH_2\dot{C}HY \quad (I) ,$$
$$ArCH_2\dot{C}HY + CuCl_2 \rightarrow ArCH_2CHYCl + CuCl .$$

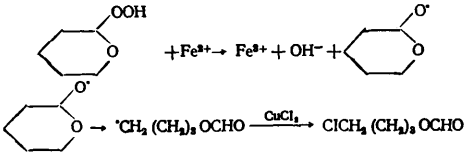
The final product $ArCH_2CHYCl$ is formed by oxidation of the radical(I) by copper(II) chloride. Addition of the aryl radical to the alkene is accompanied by the parallel reaction[77]

$$Ar\cdot + CuCl_2 \rightarrow ArCl + CuCl .$$

Occurrence of the reaction $R\cdot + CuCl_2 \rightarrow RCl + CuCl$ is indicated by the appearance of compounds containing chlorine when hydroperoxides are decomposed in aqueous solution by Fe^{2+} ions in the presence of copper(II) chloride. For example, methyl chloride is formed in the decomposition of t-butyl hydroperoxide as a result of the reactions[78]

$$(CH_3)_3COOH + Fe^{2+} \rightarrow (CH_3)_3CO\cdot + OH^- + Fe^{3+} ,$$
$$(CH_3)_3CO\cdot \rightarrow CH_3COCH_3 + \dot{C}H_3 ,$$
$$\dot{C}H_3 + CuCl_2 \rightarrow CH_3Cl + CuCl .$$

The decomposition of tetrahydropyran hydroperoxide is accompanied by the formation of $ClCH_2[CH_2]_3OCHO$ by the mechanism[78]



Similarly, the decomposition of tetrahydrofuran hydroperoxide yields $ClCH_2[CH_2]_2OCHO$ [79].

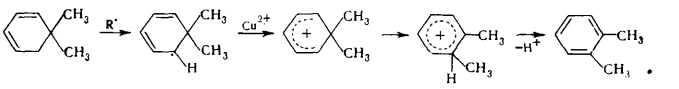
Reaction of the Type $R\cdot + M^{(n+1)+} \rightarrow R^+ + M^{n+}$

Alkyl radicals are oxidised by copper ions with formation of an alkene and an alcohol[80-82]. The carbonium ion is most probably the precursor or both products, and oxidation of the alkyl radical results from electron transfer from the radical to the copper(II) ion:

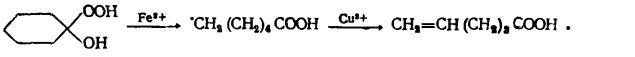
$$R\cdot + Cu^{2+} \rightarrow R^+ + Cu^{1+} ,$$
$$R^+ \rightarrow Alkene + H^+ ,$$
$$R^+ + H_2O \rightarrow ROH + H^+ .$$

In the oxidation of various radicals by copper ions the yield of alcohol is greater the more stable is the carbonium ion formed[80]: the ratio [Alcohol]/[Alkene] has the values 0.81, 3.4 and 9.1 for C_2H_5, s-C_4H_9, and t-C_4H_9 respectively, while the allyl radical is oxidised solely to the alcohol. This is consistent with the hypothesis of a carbonium ion as kinetically independent species formed in the oxidation of an alkyl radical.

Perhaps the most convincing evidence of formation of a carbonium ion is the formation of *o*-xylene from 5,5-dimethylcyclohexadiene in the presence of a peroxide (source of radicals) and copper ions[83]. This fact is explained by the following mechanism[83], involving formation of a carbonium ion:



The oxidation of alkyl radicals by copper ions is used for the preparation of certain unsaturated compounds: e.g. [82]



The thermal and photochemical decarboxylation of aliphatic (butyric, isobutyric) acids under the influence of cobalt(III) and cerium(IV) ions is accompanied by oxidation of alkyl radicals by these ions[84,85]. Evidence of this is provided by the formation of 2-methylpropene and an ester as a result of decarboxylation of pivalic acid (where $R\cdot = (CH_3)_3C\cdot$):

$$(RCOO)_3Co \rightarrow (RCOO)_2Co + RCO_2^\cdot ,$$
$$RCO_2^\cdot \rightarrow R\cdot + CO_2 ,$$
$$R\cdot + Co^{III} \rightleftarrows R'Co^{III} ,$$
$$R'Co^{III} \rightarrow R^+ + Co^{II} ,$$
$$(CH_3)_3C^+ \rightarrow (CH_3)_2C{=}CH_2 + H^+ ,$$
$$(CH_3)_3C^+ + RCOOH \rightarrow RCOOC(CH_3)_3 + H^+ .$$

In the decarboxylation of n-butyric acid the radical R· is converted mainly into RH, since the reaction $R\cdot + RCOOH \rightarrow RH + R'\cdot$ occurs more rapidly than the reaction $R\cdot + Co^{III}$ or $R\cdot + Ce^{IV}$. In the presence of copper ions, however, $n\text{-}C_3H_7\cdot$ is oxidised with the formation of propene and an ester[84,85]. Hence copper(II) ions react with alkyl radicals much more rapidly than do cobalt(III) and cerium(IV) ions, although the latter are stronger oxidants than are copper ions.

The oxidation of n-pentanol by cerium nitrate[86] gives an 11–15% yield of 2-methyloxolan. Formation of this compound can be explained by the mechanism

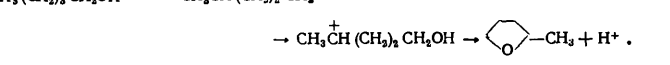


Table 3 lists rate constants for the oxidation of various alkyl radicals by copper complexes. The rate constants were measured by the method of competing reactions.

Reaction of the Type $R\cdot + M^{n+} \rightarrow R^- + M^{(n+1)+}$

Reducing ions (Ti^{3+}, V^{2+}, Cr^{2+}) are able to convert the methyl radical to the carbanion. This is proved by the

formation of DCH_3 from methyl radicals in the presence of metal ions in heavy water[82]:

$$CH_3^{\cdot} + M^{n+} \rightarrow CH_3^- + M^{(n+1)+},$$
$$CH_3^- + D_2O \rightarrow CH_3D + DO^-.$$

The experimental $[CH_4]/[CH_3D]$ ratio (methane is formed by the reaction $CH_3^{\cdot} + RH$) is lower the stronger the reductant: it has the values 2100, 32, 11, and 4.6 for Fe^{2+}, Ti^{3+}, V^{2+}, and Cr^{2+} respectively.

Table 3. Rate constants of $R^{\cdot} + CuL_4^{2+}$ reactions measured by MCR method in 1 : 1.5 CH_3CN-CH_3COOH at 25.5°C.[87]

Ion	Radical	lg*k*
$Cu(NCCH_3)_4^{2+}$	$CH_3CH_2CH_2CH_2^{\cdot}$	6.49
$Cu(C_{10}H_8N_2)^{2+}$	$CH_3CH_2CH_2CH_2^{\cdot}$	7.23
$Cu(NCCH_3)_4^{2+}$	$(CH_3)_3CCH_2^{\cdot}$	5.65
$Cu(C_{10}H_8N_2)^{2+}$	$(CH_3)_3CCH_2^{\cdot}$	4.40
$Cu(NCCH_3)_4^{2+}$	$C_6H_5CH_2CH_2^{\cdot}$	6.20
$Cu(C_{10}H_8N_2)^{2+}$	$C_6H_5CH_2CH_2^{\cdot}$	7.145
$Cu(NCCH_3)_4^{2+}$	p-$CH_3OC_6H_4CH_2CH_2^{\cdot}$	4.32
$Cu(C_{10}O_2N_2)^{2+}$	p-$CH_3OC_6H_4CH_2CH_2^{\cdot}$	6.48
$Cu(NCCH_3)_4^{2+}$	$(CH_3)_2CH^{\cdot}$	6.70

Complexes of the Type $(R{\cdot}M)^{n+}$

Kochi and Rust studied the decomposition of t-butyl hydroperoxide in aqueous solution, and found that the yield of ethane increased in the presence of ions of metals with variable valency[88]: the ratio $[C_2H_6]/[CH_4] = 0.33$ in the absence of ions, and increases to 0.95, 0.95, and 4.9 in the presence of Mn^{2+}, Co^{2+}, and Ni^{2+} respectively. The yield of ethane in the presence of Fe^{2+} decreases with increasing concentration of F^- ions, which form a complex with Fe^{2+}. A similar phenomenon is observed if ethyl radicals are generated in the solution[88]: the ratio $[C_4H_{10}]/[C_2H_6]$ has the values 0.27 in the absence of metal ions, 1.05 in the presence of Co^{2+}, and 1.17 in the presence of Ni^{2+}. This result was explained by complex formation:

$$R^{\cdot} + M^{n+} \rightleftharpoons (R^{\cdot}M)^{n+},$$
$$R^{\cdot} + (R \cdot M)^{n+} \rightarrow R{-}R + M^{n+},$$
$$2(R \cdot M)^{n+} \rightarrow R{-}R + 2M^{n+}.$$

The alkyl radical is less active in the complex; this lowers the yield of methane in the case of methyl radicals, and of ethane in the case of ethyl radicals.

A similar conclusion was reached by Brackman and his coworkers in a study of the products of the radiolysis of methanol[89]. In the absence of metal ions the oxidising radicals formed by radiolysis combine rapidly to give ethylene glycol: $2{\cdot}CH_2OH \rightarrow HOCH_2CH_2OH$. In the presence of metal ions formaldehyde is produced, its appearance being explained by complex formation:

$$^{\cdot}CH_2OH + M^{n+} \overset{K}{\rightleftharpoons} (\dot{M}CH_2OH)^{n+},$$
$$(\dot{M}CH_2OH)^{n+} + {}^{\cdot}CH_2OH \overset{k}{\rightarrow} CH_2O + CH_3OH + M^{n+}.$$

The products kK of these constants calculated from the experimental results at 30°C have the values:

Ion:	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
kK:	0.043	0.124	4.87	3.13	15.6	0.215

5. REACTIONS OF MACRORADICALS WITH IONS OF METALS HAVING VARIABLE VALENCY

The introduction of ions of variable valency into a system in which radical polymerisation is occurring results in retardation of the chain polymerisation owing to the termination of chains by interaction between macroradicals and metal ions. Termination takes place both on oxidising ions (Fe^{3+}, Cu^{2+}, $CeOH^{3+}$) and on reducing ions (Cr^{2+}, V^{2+}, Ti^{3+}). The mechanism of chain polymerisation in the presence of inhibitor ions can be

Table 4. Rate constants for reactions of macroradicals with metal ions.

Ion	Conditions	Temp., [°C]	lg*k*	lg*A*	*E*	Ref.
	Radical CH_2-$CHCINH_2$					
Ti^{3+}	D_2O, 0.0,8H_2SO_4	25	2.91	—	—	90
Ti^{3+}	H_2O, 0.8 H_2SO_4	25	2.76	12.0	11.1	90
Ti^{3+}	H_2O, 1M $HClO_4$	25	1.28	12.0	14.6	91
VO_2^+	H_2O, 0.08 N H_2SO_4	25	3.04	—	—	90
V^{3+}	H_2O, 0.08 N H_2SO_4	25	5.04	—	—	90
Cr^{3+}	H_2O, 0.08 N H_2SO_4	25	5.45	—	—	90
Fe^{3+}	H_2O, pH=1	25	3.30	—	—	92
Fe^{3+}	H_2O, 1M $HClO_4$	25	3.45	5.16	2.35	91
Fe^{3+}	D_2O, 1M $HClO_4$	25	3.41	5.20	2.44	91
$FeOH^{2+}$	H_2O —	25	4.04	—	—	92
$FeOH^{2+}$	H_2O —	25	4.325	—	—	90
$FeCl^{2+}$	H_2O —	25	4.91	—	—	90
$FeCl_2^+$	H_2O —	25	4.23	—	—	90
$FeCl_3$	H_2O —	25	6.00	—	—	90
$FeBr^{2+}$	H_2O —	25	6.22	—	—	90
FeN_3^{2+}	H_2O —	25	6.19	—	—	90
$FeCNS^{2+}$	H_2O —	25	7.13	—	—	90
$Fe(bipy)_3^{3+}$	H_2O	25	4.91	—	—	90
Fe (*o*-phen)$_3^{3+}$	H_2O	25	5.49	—	—	90
Fe (5-CH_3-*o*-phen)$_3^{3+}$	H_2O	25	5.415	—	—	90
Fe (5-C_6H_5-*o*-phen)$_3^{3+}$	H_2O	25	5.71	—	—	90
Fe (5-Cl-*o*-phen)$_3^{3+}$	H_2O	25	5.36	—	—	90
$Fe(CN)_6^{3-}$		25	5.93	—	—	90
Cu^{2+}	H_2O. I M $HClO_4$	25	3.07	7.04	5.4	91
Cu^{2+}	D_2O. I M $HClO_4$	25	3.145	7.00	5.3	91
Mo^{3+}	D_2O. I M $HClO_4$	25	3.845	—	—	90
$CeOH^{2+}$	H_2O. I M $HClO_4$	25	3.51	5.30	2.45	91
Eu^{3+}	H_2O, 0.8 H_2SO_4	25	4.925	—	—	90
Hg^{2+}	H_2O, 0.1 M $HClO_4$	25	0.02	4.62	6.2	91
Ti^{3+}	H_2O, 0.1 M $HClO_4$	25	1.53	1.32	2.5	91
Fe^3	H_2O	25	1.725	7.4	7.7	93
$FeOH^{2+}$	H_2O	25	3.24	11.3	11	93
(Fe — $NH_2COC(CH_2)$ = = CH_2)$^{2+}$	H_2O	25	3.785	7.7	5.5	93
	Radical ~CH_2-C·HCN					
$Fe(CN)_6^{3-}$	H_2O	25	6.83	—	—	94
$FeCl_3$	CHON $(CH_3)_2$	25	3.81	—	—	95
$FeCl_3$	CHON $(CH_3)_2$	25	3.91	—	—	96
	radical ~ CH_2 — Ċ (CH_3) CN					
$FeCl_3$	CHON $(CH_3)_2$	25	2.79	—	—	95
	radical ~ CH_2 CHC_6H_5					
$FeCl_3$	CHON $(CH_3)_2$	25	4.73	—	—	95
	radical ~ CH_2Ċ (CH_3) $COOCH_3$					
$CuCl_2$	CHON $(CH_3)_2$	60	5.89	—	—	97

represented by the simple scheme (where M is the monomer [and Me the metal])

$$\text{Initiator} \rightarrow r^{\cdot} \xrightarrow{M} M^{\cdot},$$
$$M^{\cdot} + M \xrightarrow{k_p} M^{\cdot},$$
$$M^{\cdot} + M^{(n+1)+} \xrightarrow{k_x} M^{+} + M^{n+},$$
$$M^{+} + H_2O \rightarrow MOH + H^{+},$$
$$M^{+} \rightarrow \text{Alkene} + H^{+}.$$

The rate of polymerisation in this system is $w = k_p[M^{\cdot}][M] = k_p[M]w_i/k_x[Me^{(n+1)+}]$ (where w_i is the rate of initiation). Measurement of the rate of polymerisation at different ionic concentrations gives the ratio of the constants k_p/k_x, and values of k_x are calculated for known values of k_p (this method has been used for the k_x in Table 4).

If values of $\lg k$(Radical + Fe^{III}) are compared for H· (Table 1) and ~$CH_2CHCONH_2$ (Table 4), where Fe^{III} reacts in the forms Fe^{3+}, $FeOH^{2+}$, $FeCl^{2+}$, a linear relation is observed:

$$\lg k(\sim CH_2CHCONH_2) = -3.2 + 0.835 \lg k(H).$$

6. REACTIONS OF PEROXY-RADICALS WITH COMPOUNDS OF METALS HAVING VARIABLE VALENCY

Salts of metals with variable valency are widely used as catalysts for the liquid-phase oxidation of hydrocarbons. The primary reason for their accelerating action on oxidation is that they break down hydroperoxides to form free radicals, and thus ensure that a chain oxidation shall be rapid. In some cases, however, salts of metals having variable valency behave as inhibitors: they retard oxidation. This is due to the termination of chains as a consequence of reactions between peroxy-radicals and the lower-valency form of the catalyst[98]: e.g.

$$RO_2^{\cdot} + St_2Co \rightarrow St_2CoOH + R'{=}O,$$
$$RO_2^{\cdot} + St_2Mn \rightarrow St_2MnOH + R'{=}O.$$

The inhibiting effect of cobalt and manganese stearates on the oxidation of cyclohexane[93], α-pinene[99], synthin[100], n-octane[101], and n-decane[102] is observed only if the catalyst is added in sufficiently high concentration (when $k[St_2Co][RO_2^{\cdot}] > k_6[RO_2^{\cdot}]^2$) in the lower valency state (Co^{III} and Mn^{III} do not retard oxidation) and if it is added at the start of oxidation (when hydroperoxide is absent, and the catalyst does not take part in the initiation of chains). During the oxidation the retarding effect of the catalyst usually disappears, firstly because a hydroperoxide has appeared and the catalyst is involved in chain initiation, and secondly as a reaction of the type $RO_2^{\cdot}$ + Co^{II} → Mol. products + Co^{III} ceases to cause chain termination, for Co^{III} immediately reacts with an oxidation product of the hydrocarbon (alcohol, ketone, or aldehyde) to form a free radical. Thus during an oxidising process the reactions between peroxy-radicals and the catalyst are converted from chain-terminating steps into chain-propagating steps involving the catalyst. This explains also the influence of the catalyst on the composition of the oxidation products of the hydrocarbons cyclohexane[103], n-decane[102], and alkanes[104]. This aspect has been discussed in detail in a review[105] and in a monograph[4].

Critical phenomena characteristic of the inhibited oxidation of hydrocarbons[106] are observed also in catalysed oxidations. A detailed study of this phenomenon has been made by Gol'dberg and Obukhova on the oxidation of n-decane in the presence of a potassium–manganese catalyst[107-109]. When a mixture of potassium and manganese stearates is added to n-decane undergoing oxidation, more prolonged inhibition is observed than in the case of manganese stearate alone. The induction period is directly proportional to $[KSt.MnSt_2]^3$. This is explained by formation of the strongly inhibiting complex $3KSt.3MnSt_2$ [107]. Complex formation is proved by electron spin resonance. A critical phenomenon is observed on the introduction of the potassium–manganese catalyst into oxidised n-decane containing a hydroperoxide[108]. When the hydroperoxide content of the decane was less than 2.3 mole % (at 140°C), addition of the catalyst was found to halt the process; but when the hydroperoxide content exceeded this value, the reaction was rapidly accelerated. The occurrence of a critical hydroperoxide concentration in this system is due to the fact that the catalyst initiates chains by reacting with the hydroperoxide at a rate $k_i[St_2Mn][ROOH]$ and terminates chains[108] by the reaction of peroxy-radicals with the complex $3KSt.3MnSt_2$.

In the course of the catalytic oxidation of n-decane the process ceases after some time. A linear relation is observed between the catalyst and hydrocarbon concentrations at this point[109]: in other words, there is a critical ratio between the concentration of the K–Mn catalyst and that of the hydrocarbon in the catalysed oxidation of n-decane.

Hence reactions of peroxy-radicals with compounds of metals having variable valency play a very important part in the mechanism of catalysed liquid-phase oxidation.

In a hydrocarbon medium peroxy-radicals react rapidly with a salt of a metal with variable valency. The rate constant for the reaction of manganese stearate with the peroxy-radical $(CH_3)_2(CN)COO\cdot$ in chlorobenzene measured by a chemiluminescent method is[110]

$$k = 2.8 \cdot 10^8 \exp(-4800/RT)\ M^{-1}\,s^{-1}.$$

The rate constant for the reaction between cobalt(II) acetylacetonate and peroxy-radicals of styrene $C_6H_5CH(OO\cdot)CH_2\sim$ in chlorobenzene is[111]

$$k = 2.9 \cdot 10^9 \exp(-7800/RT)\ M^{-1}\,s^{-1}.$$

The peroxy-radical most probably adds to the cation of the salt of the metal with variable valency, and is then converted into stable molecular products. It has been established[112] that a ketone is formed by reaction of a secondary peroxy-radical with manganese stearate, so that we can write the mechanism

$$RO_2^{\cdot} + MnSt_2 \rightarrow ROO{-}MnSt_2 \rightarrow HOMnSt_2 + R'{=}O.$$

A different type of reaction takes place between the peroxy-radical and the metal complex if the latter contains a ligand having a labile O–H or N–H bond. In this case the peroxy-radical reacts with the ligand as with an ordinary inhibitor. When copper stearate and phenyl-2-naphthylamine are added together to n-decane undergoing oxidation, they cause prolonged inhibition of the reaction[113]; the amine inhibitor is consumed rapidly, but oxidation is inhibited for many hours after it has been exhausted. The explanation offered is that the amine forms with the copper stearate a complex which has a strongly inhibiting action by reacting rapidly with the peroxy-radicals:

$$R_1R_2NH + CuSt_2 \rightleftharpoons StH + StCu\dot{N}R_1R_2,$$
$$RO_2^{\cdot} + St_2Cu\dot{N}R_1R_2 \rightarrow \text{Mol.products}.$$

Study of the inhibiting action of hydroxyquinoline complexes of metals on the oxidation of ethylbenzene[114] has provided kinetic evidence of the reaction of a peroxy-radical with a ligand in the complex. It was established by a chemiluminescent method that, with excess of hydroxyquinoline in the system, chains were terminated by reaction between peroxy-radicals and the metal–hydroxyquinoline complex, whereas the duration of the inhibition was determined by the concentration of hydroxyquinoline OxH in the solution. This corresponds to the following mechanism of inhibition:

$$M^{n+} + OxH \rightleftharpoons MOxH^{n+},$$
$$RO_2^{\cdot} + MOxH^{n+} \rightarrow ROOH + MOx^{n+}.$$

It is interesting that free hydroxyquinoline has a very weak inhibiting effect on oxidation, whereas its complexes react rapidly with peroxy-radicals.

It has been established[115] that the oxidation of cumene is inhibited by the complex of cobalt with dimethylglyoxime DM of composition $Co(DM)_2pyCl$. In this case, too, the peroxy-radical probably reacts with an O–H bond of dimethylglyoxime in the complex.

In contrast to the peroxy-radicals from hydrocarbons, the hydroperoxy-radical $HO_2\cdot$ is able to react either as oxidant or as reductant with ions of variable valency[116]:

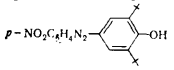
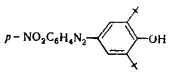
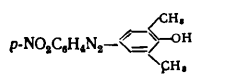
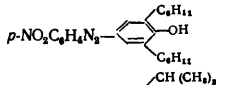
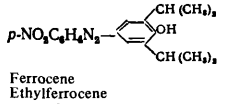
$$HO_2^{\cdot} + Fe^{2+} \rightarrow HO_2^{-} + Fe^{3+},$$
$$HO_2^{\cdot} + Fe^{3+} \rightarrow O_2 + H^+ + Fe^{2+}.$$

The hydroxyperoxy-radical formed in the oxidation of an alcohol possesses similar dual reactivity[117]. As a consequence, copper ions are ideal negative catalysts for the chain oxidation of alcohols, which they inhibit for an infinite time[117]. The usual inhibitors are consumed during oxidation, and inhibition ceases when the inhibitor is exhausted. Negative catalysis by copper ions in an alcohol undergoing oxidation is due to the reactions

$$>C(OH)OO\cdot + Cu^{2+} \rightarrow >C{=}O + O_2 + H^+ + Cu^{1+},$$
$$>C(OH)OO\cdot + Cu^{1+} \rightarrow >C(OH)OO^- + Cu^{2+},$$
$$>C(OH)OO\cdot + H^+ \rightleftharpoons >C(OH)OOH \rightleftharpoons >C{=}O + H_2O_2.$$

Table 5 lists rate constants for the reactions of peroxy-radicals with ions and complexes of metals of variable valency. The $HO_2\cdot$ + Ion rate constants were measured by the pulse radiolysis method, except in the case of the reaction $Cu^+ + HO_2\cdot$, whose rate constant was measured by a flow method[118]. The rate constants for the reactions of peroxy-radicals with metal complexes were determined by chemiluminescence methods[114,119], except in the cases of the $RO_2\cdot$ + $Co(acac)_2$ reaction, where the rate of consumption of Co^{II} was determined[107], and the $RO_2\cdot$ + Cu^{2+} reaction, where the rate constant was calculated from the dependence oxidation of the rate on the concentration of copper ions[117].

Table 5. Rate constants for reactions of peroxy-radicals with ions and complexes of metals.

Ion	Conditions	Temp., [°C]	lg k	Ref.
	Radical $HO_2\cdot$			
Fe^{2+}	H_2O, 0.5 *M* H_2SO_4	23	5.86	120
Fe^{3+}	H_2O, pH = 2.05	25	5.52	121
Cu^{2+}	H_2O, pH = 2.3	23	7.18	122
Cu^{2+}	H_2O	25	8.04	118
Cu^{1+}	H_2O	25	9.63	118
MnO_4^-	H_2O, pH = 3	23	6.90	33
Br_2^-	H_2O	23	9.175	123
Br_2^-	H_2O	23	9.58	123
Br_2^-	H_2O	23	9.20	124
Br_2^-	H_2O	23	8.00	124
CNS^-	H_2O, pH = 1	23	9.20	60
	Radical $C_6H_5CH(CH_3)OO\cdot$			
Mn EDTA^{2-}	$CH_3COOH + C_6H_5CH_2CH_3$	60	6.00	114
Co EDTA^{2-}	$CH_3COOH + C_6H_5CH_2CH_3$	60	5.58	114
Co (Oxin)$_2$	$CH_3COOH + C_6H_5CH_2CH_3$	60	7.955	114
Cu (Oxin)$_2$	$CH_3COOH + C_6H_5CH_2CH_3$	60	5.90	114
Mn (Oxin)$_2$	$CH_3COOH + C_6H_5CH_2CH_3$	60	5.62	114
Ni (Oxin)$_2$	$CH_3COOH + C_6H_5CH_2CH_3$	60	5.35	114
Mn^{2+} complexes of azo-compounds				
	$CH_3COOH + C_6H_5CH_2CH_3$	60	5.575	114
	$CH_3COOH + C_6H_5CH_2CH_3$	60	6.52	114
	$CH_3COOH + C_6H_5CH_2CH_3$	60	7.29	114
	$CH_3COOH + C_6H_5CH_2CH_3$	60	7.48	114
	$CH_3COOH + C_6H_5CH_2CH_3$	60	5.96	114
Ferrocene	$CH_3COOH + C_6H_5CH_2CH_3$	60	5.38	119
Ethylferrocene	$CH_3COOH + C_6H_5CH_2CH_3$	60	5.255	119
Phenylferrocene	$CH_3COOH + C_6H_5CH_2CH_3$	60	4.92	119
Acetylferrocene	$CH_3COOH + C_6H_5CH_2CH_3$	60	4.52	119
Cyanoferrocene	$CH_3COOH + C_6H_5CH_2CH_3$	60	3.60	119
Ferrocenecarboxylic acid	$CH_3COOH + C_6H_5CH_2CH_3$	60	4.08	119
	Радикал $(CH_3)_2(CN)COO\cdot$			
Mn $[OOC(CH_2)_{16}CH]_2$	C_6H_5Cl	70	5.38	110
Co $(acac)_2$	C_6H_5Cl	74	4.36	111
	Radical $\sim CH_2CH(C_6H_5)OO\cdot$			
Co $(acac)_2$*	C_6H_5Cl	55–85	4.69 (80°)	111
	Радикал			
Cu^{2+}	cyclo-$C_6H_{11}OH$ + 10% H_2O	75	6.505	117

* The following abbreviations have been adopted:

EDTA = $(-OOC)_2NCH_2CH_2N(COO^-)_2$; Oxin =

acac = $CH_3C(O^-)=CH-C(=O)CH_3$

7. OXIDATION OF FERROUS IONS BY DIPHENYLPICRYLHYDRAZYL

Several studies have been made of the oxidation of Fe^{2+} ions by diphenylpicrylhydrazyl[121–123]. In aqueous alcohol the rate constant of this bimolecular reaction is $2.7 \times 10^{11} \exp(-13\,500/RT)$ and $1.2 \times 10^8 \exp(-8100/RT)$ $M^{-1}\,s^{-1}$ for alcohol contents of 50%[125] and 80%[126] respectively.

It is assumed that a hydrogen atom is abstracted by the radical from a ligand (alcohol molecule)[125]:

$$R^{\cdot} + Fe(ROH)_n^{3+} \rightarrow RH + [Fe(ROH)_{n-1}RO]^{2+}.$$

8. REACTIONS OF OTHER RADICALS WITH IONS

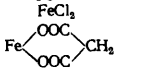
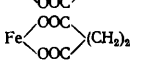
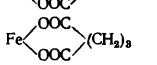
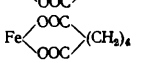
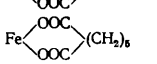
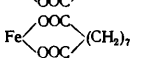
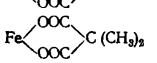
Alkoxy-radicals are oxidants and react with reducing ions. When t-butyl hydroperoxide decomposes in the presence of reducing cations in solution, t-butyl alcohol is formed[128]. This indicates that the reaction

$$(CH_3)_3CO^{\cdot} + M^{n+} \rightarrow (CH_3)_3CO^{-} + M^{(n+1)+}$$

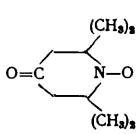
occurs in parallel with the breakdown of $(CH_3)_3CO\cdot$ into acetone and a methyl radical. Values of the [Alcohol]/-[Acetone] ratio are given below for various reducing ions[128]:

Ion	Ti^{3+}	Fe^{2+}	Cr^{3+}	V^{3+}	$Fe(CN)_6^{4-}$	S_4O_6
[Alcohol]/[Acetone]	0.59	1.0	4.26	1.0	9.0	19

Table 6. Oxidation of iron ions by diphenylpicrylhydrazyl.

Ion	Conditions	Temp., °C	lg$k$	Ref.
Fe^{2+}	$H_2O:C_2H_5OH = 1:1$	20	1.36	125
Fe^{2+}	$H_2O:C_2H_5OH = 1:4$	20	2.03	126
Fe^{2+}	CH_3OH	22.5	2.825	127
$FeCl_2$	CH_3OH	22.5	5.565	127
Fe^{2+}	C_2H_5OH	22.5	1.46	127
$FeCl_2$	C_2H_5OH	22.5	2.875	127
Fe^{2+}	n-C_3H_7OH	22.5	1.505	127
$FeCl_2$	n-C_3H_7OH	22.5	3.85	127
Fe^{2+}	$(CH_3)_2CHOH$	22.5	2.00	127
$FeCl_2$	$(CH_3)_2CHOH$	22.5	3.70	127
Fe^{2+}	n-C_4H_9OH	22.5	1.505	127
$FeCl_2$	n-C_4H_9OH	22.5	3.59	127
Fe^{2+}	n-$C_5H_{11}OH$	22.5	1.20	127
$FeCl_2$	n-$C_5H_{11}OH$	22.5	3.54	127
Fe^{2+}	n-$C_7H_{15}OH$	22.5	1.84	127
$FeCl_2$	n-$C_7H_{15}OH$	22.5	3.475	127
	n-C_4H_9OH 0.05 M $NaClO_4$	20	3.33	127
	n-C_4H_9OH 0.05 M $NaClO_4$	20	2.195	127
	n-C_4H_9OH 0.05 M $NaClO_4$	20	2.04	127
	n-C_4H_9OH 0.05 M $NaClO_4$	20	1.895	127
	n-C_4H_9OH 0.05 M $NaClO_4$	20	1.875	127
	n-C_4H_9OH 0.05 M $NaClO_4$	20	1.855	127
	n-C_4H_9OH 0.05 M $NaClO_4$	20	2.095	127

The reaction of the nitroxide radical



with iron ions has been studied[129]. In the presence of 0.1M HCl and 0.4M NaCl in water the rate constant is

$$k = 8.1 \cdot 10^{10} \exp(-7000/RT)\ M^{-1}\ s^{-1}\ .$$

The active radical $\cdot NO_3$ is a strong oxidant, and oxidises Ce^{3+} to Ce^{4+}. At 23 °C the rate constant of this reaction is $1.70 \times 10^6\ M^{-1}\ s^{-1}$, with $E = 1$ kcal mole^{-1}.[130]

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Great success has been achieved by chemical kinetics during recent years in the quantitative investigation of rapid ion–radical reactions involving such species as H·, HO·, $HO_2\cdot$, and macroradicals. With few exceptions, however, the detailed mechanism of such reactions still remains obscure. An atom (a radical) may react with an ion after an intermediate stage involving substitution of a ligand in the inner coordination sphere, it may react with one of the ligands of the complex (by detaching an atom or adding to the ligand), or finally electron transfer may occur through the solvent. As is evident from the present Review, a conclusion can be reached in some cases, but in many cases the detailed mechanism of interaction between radicals and ions is obscure. A more profound understanding of the mechanism of these reactions will require elucidation of the effect of the solvent and of the ionic strength on ion–radical reactions. It is also important to know the activation energy of these reactions (in most cases the rate constants have been measured at a single temperature).

A very promising field of investigation is the formation of complexes between metal ions and free radicals. As yet such complex formation can be judged only from the changed composition of the products from radicals in the presence of ions. Such complexes are obviously short-lived labile structures. Some of them, of course, possess unusual reactivity for free radicals. Investigation of the reactions of such complexes, e.g. by a flow method, is of undoubted scientific interest.

Hardly any quantitative study has yet been made of the reactions of many radicals with ions of metals of variable valency. Such radicals include, for example, alkyl, phenyl, alkoxyl, carboxyl, and hydroxyalkyl radicals. The lack of quantitative data on the rate of these reactions does not permit assessment of their role or value in various transformations of organic compounds in the presence of ions.

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Advances in the Chemistry of Aliphatic *N*-Nitrosamines

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The review gives for the first time a systematic account of the extensive literature data on the chemistry of aliphatic nitrosamines. A separate chapter summarises the work on the physical properties, structure, and spectra of *N*-nitroso-derivatives. The chemical behaviour of the nitrosamines is determined largely by the characteristics of the *p*-π-conjugation in the $\rangle\ddot{N}-\ddot{N}-O$ fragment. The principal chemical reactions of nitrosamines are treated from this standpoint: the denitrosation reaction, the formation of complexes, the cyclisation to sydnones and sydnoneimines, and the synthesis of lactams. In conclusion, certain aspects of the practical applications of nitrosamines are considered.
The bibliography includes 272 references.

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I. INTRODUCTION

N-Nitrosamines occupy an important place in the large class of nitroso-compounds. The reason for this is not only the high chemical reactivity of the nitroso-group but also the valuable products formed as a result of various reactions. It is sufficient to say that *N*-nitroso-compounds are widely used in the synthesis of diazo-derivatives and dialkylhydrazines, and are employed to prepare nitramines, sydnones, sydnoneimines, and complex compounds. The *N*-nitrosation reaction is closely related to the chemistry of carbonium ions. *N*-Nitrosamines are excellent objects for the investigation of *p*-π-conjugation, n-π^* and π-π^* transitions, and rotational isomerism.

Despite the large number of studies that have been made on nitrosamines and their theoretical and practical importance, we were unable to find any reviews on this field of chemistry. The existing reviews deal mainly with aromatic nitrosamines, or deal with highly specific problems [1-5].

The present review is the first attempt to fill this gap, and covers the fundamental studies on aliphatic nitrosamines up to 1968-1969.

The study of the chemistry of aliphatic nitrosamines began in 1863, when Geuther obtained *N*-nitrosodiethylamine by the reaction of diethylamine hydrochloride with sodium nitrite [6,7]. Subsequently the *N*-nitrosation reaction was employed by many investigators, who improved and developed it. A number of interesting studies on the chemistry of nitrosamines have been made by Soviet chemists. Significant advances in the understanding of the structure of nitrosamines were made in the 1950's and 1960's. During this period, many new reactions of nitrosamines were discovered.

II. NITROSATING AGENTS AND NITROSATION

It is believed that nitrosation is achieved by agents related to nitrous acid having the structure NOX, where X = OAlk, NO_2, NO_3, halogen, or OH_2^+. Depending on the experimental conditions, any member of this series may become the main nitrosating agent.

In the reaction of alkali metal nitrites with inorganic acid, nitrous acid is formed, its subsequent fate being determined by the reaction conditions. Thus two nitrous acid molecules can be converted via a stage involving "self-protonation" and nucleophilic attack by the nitrite ion into nitrogen trioxide, which is 6–10 times weaker than protonated nitrous acid [8,9]:

$$2HONO \rightleftarrows H_2\overset{+}{O}\cdot NO + NO_2^-,$$

$$H_2\overset{+}{O}\cdot NO + NO_2^- \rightleftarrows N_2O_3 + H_2O.$$

If a halide ion serves as the nucleophilic agent, nitrosyl halides are formed. This happens when the nitrosation is carried out in hydrogen halide solution [10,11].

In a highly acidic medium, nitrogen trioxide and nitrous acid cannot exist in a free form, and, for example in 70–80% sulphuric acid, are converted into the nitrosonium salt $NO^+HSO_4^-$. [12] Nitrosyl sulphate acid readily dissociates with formation of a nitrosonium cation [13]:

$$N_2O_3 + 3H_2SO_4 \rightarrow 2NO^+ + 3HSO_4^- + H_3O^+.$$

The nitrosonium cation is one of the most active nitrosating agents. Nitrosonium tetrafluoroborate is an interesting nitrosating substance [14]. Recently nitrosylsulphuric anhydride $HOSO_2ONO$ was proposed as an effective nitrosating compound [15].

Certain investigators [16] explain the nitrosating activity of nitrogen tetroxide by the existence of the latter in the nitrosyl nitrate form $NO.ONO_2$, which serves as a source of nitrosonium cations, like the nitrosonium salt of sulphuric acid already mentioned. The nitrosonium cation is present at high concentrations only at high acidities. In a weakly acidic medium or in the presence of an active nucleophilic agent, for example hydroxide ions, the nitrosonium cation is converted into nitrous acid and further into nitrite ions [13]:

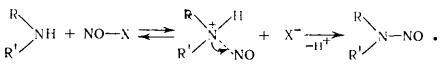
$$NO^+ + OH^- \rightleftarrows HNO_2 \rightleftarrows H^+ + NO_2^-.$$

At pH $\geqslant$ 7 the equilibrium in the reaction is completely displaced to the right.

Depending on changes in the acidity in the reaction zone, various nitrosating agents are present, which can be arranged in the following series in terms of increasing activity [11]: $NO.NO_2$, NOCl(Br, F), $NO.OH_2^+$, NO^+. Nitrous

acid and alkyl nitrites are absent from this series because free nitrous acid does not exhibit nitrosating activity [11]. In addition nitrous acid salts of primary and secondary amines have been described in a number of papers [17,18]. Alkyl nitrites are as a rule rarely recommended for *N*-nitrosation reactions.

In its simplest form the nitrosation of amines includes electrophilic attack by the nitrosating species on the lone pairs of sp^3 electrons of the nitrogen atom and subsequent deprotonation of the alkylnitrosimmonium cation [11]. In the case of secondary dialkylamines the reaction may be represented by the following scheme:



The amine participates in the reaction in a non-protonated form and therefore it is desirable to carry out the nitrosation of highly basic amines in a weakly acidic medium. Under these conditions, the comparatively inactive nitrogen trioxide or at best a nitrosyl halide will function as the nitrosating agent. With amines having a low electron density at the nitrogen atom, nitrogen trioxide proved to be less effective than the nitrosonium cation. This makes it necessary to carry out the reaction in a highly acidic medium.

Thus the acidity of the medium plays a dual role in the nitrosation of amines. Its increase enhances the concentration of the more powerful nitrosating agent ($H_2O^+.NO$, NO^+), but lowers the concentration of the active (non-protonated) form of the amines, i.e. the excess acid has an inhibiting effect, which is shown particularly clearly in the case of highly basic aliphatic amines. When the basicity of the amine is low, part of it may exist as the non-protonated species even in the presence of a considerable excess of the acid [11] and this species is in fact acted upon by the powerful nitrosating agent.

These factors must be taken into account in the nitrosation of various types of secondary amines.

III. METHODS OF SYNTHESIS OF *N*-NITROSAMINES

The methods of preparation of *N*-nitrosamines may be divided into three principal groups: 1) nitrosation of secondary amines in an acidic medium, which should include also the nitrosation of the hydrochlorides, hydrogen nitrates, and hydrogen sulphates of secondary amines by metal nitrites; 2) nitrosation with the aid of NOCl, N_2O_3, and N_2O_4; 3) nitrosation by cleaving tertiary amines. In addition, several methods of nitrosation have been described which are not of general importance at the present time.

1. Reaction of Alkali Metal Nitrites with Solutions of Amines in Acids

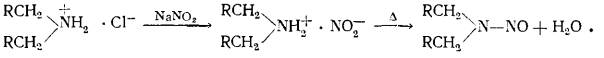
After the discovery of *N*-nitrosodialkylamines [6] the efforts of investigators were concentrated on the development of a convenient and reliable method for their synthesis. As early as 1865, Fischer found that, when dimethylamine hydrochloride acidified with sulphuric acid is treated with sodium nitrite in an aqueous medium, *N*-nitrosodimethylamine is formed in a high yield [19]. Subsequently acetic [20-25] or nitric [26-29] acid was employed in addition to sulphuric acid, but hydrochloric acid in fact found the widest application [30-51].

Various modifications of Fischer's method are distinguished by the procedures employed to isolate the desired products or by the temperature conditions. Nitrosamines have been extracted from the reaction medium by steam distillation [19,52-54], extraction by different solvents [20,21,30,37,50], and other methods [6,20,21,31-36]. Some investigators carried out the nitrosation reaction with cooling (usually to 0–5 °C), [20,27,36,40,41,45-51,55-58] while others heated the reaction mixture [6,22,31,36,38,52,54,59-61]. However, temperature is in fact an important factor in the reaction. In an acidic medium it is desirable to carry out the process at a low temperature to avoid denitrosation, which is acid-catalysed. If the acidity in the reaction zone is low, the process usually takes place at an elevated temperature [60,61], which has a favourable effect on the yield of the final product and reduces the duration of the reaction. It is not fortuitous that, in the synthesis of nitrosamines, many investigators treated secondary amine hydrochlorides with an excess of sodium or potassium nitrite at room or higher temperature without additional acidification [6,21,37,55,59,62-69].

By virtue of its simplicity, nitrosation in an acidic medium has been more widely used than other methods [70-72]. The considerable range of applications of "acid" nitrosation is shown by its employment to synthesise many nitrosamines containing various substituents in the alkyl residue: aryl groups [23,35,36,39,57,63,73-75], halogens [21,59,76,77] and keto- [22,41,64], ester [32-34,62,78,79], carboxy- [37,40,45,50,56], hydroxy- [21,57,61,73], alkoxy- [20,53], nitrile [26,46-49,51,78,80], nitrate [27], sulphate [81], and nitro-groups [55]. Nitrosation in an aqueous solution of an inorganic acid has been used to synthesise dinitroso-compounds based on *N*-alkyl-substituted ethylenediamines [30,68] and nitrosamines containing an olefinic residue at the nitrogen atom [22,82]. In acetic acid a number of labelled [^{14}C]-*N*-nitrosodialkylamines have been synthesised [83].

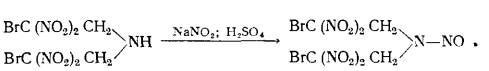
Taylor and Price [84] attempted to determine the concentration of nitrous acid necessary for successful reaction. They showed for dimethylamine that, when equimolar amounts of the reagents (0.05 *N* amine + 0.05 *N* HNO_2) are mixed, the reaction does not occur. With increase of the concentration of nitrous acid to 0.1 *N*, an adduct with the composition $[(CH_3)_2NH_2]^+.[NO_2]^-.[HNO_2]$ is formed, but the formation of *N*-nitrosodimethylamine was not observed.

The formation of nitrous acid salts in the reaction between secondary α-arylamine hydrochlorides and sodium nitrite in ethanol was observed even earlier by Curtius [17,85,86]. On prolonged refluxing in ethanol, the nitrite salt of the amine is converted into the corresponding nitrosamine:



Ring-substituted *N*-nitrosodibenzylamines have been synthesised in this way. Some investigators employed silver nitrite instead of sodium nitrite [87,88]. The results of the studies quoted [17,84-88] confirm that in the nitrosation of fairly basic amines the reaction must be carried out at comparatively high temperatures.

The dependence of the reaction conditions on the basicity of the amine is also illustrated, for example, by *N*-nitrosodi-(2-bromo-2,2-dinitroethyl)amine, which was obtained by treating di-(2-bromo-2,2-dinitroethyl)amine with sodium nitrite in concentrated sulphuric acid [29]:



In trifluoroacetic acid and trifluoroacetic anhydride, *N*-nitrosodi-(2,2,2-trinitroethyl)amine was obtained from di-(2,2,2-trinitroethyl)amine [89].

In contrast to the work of Curtius and Taylor, in the studies quoted above the nitrosation of weakly basic amines was investigated and the reaction carried out in a strongly acidic medium.

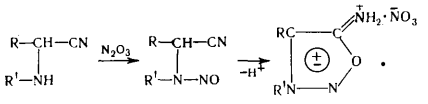
2. Reaction of Nitric Oxide, Nitrogen Trioxide, Nitrogen Tetroxide, and Nitrosyl Chloride with Secondary Amines

The first studies where the application of nitrogen trioxide as the nitrosating agent in the series of aliphatic amines was reported were carried out towards the end of the nineteenth century. Paulman [90], who investigated the properties of sarcosine, found that it reacts readily with "gaseous nitrous acid", forming a nitroso-derivative. Subsequently nitrosiminodiacetic acid [91,92] and di-(2-azapropyl-2-nitroso-3-phenyl)methanol [93] were synthesised in a similar way. The reaction was carried out in an aqueous medium:

$$(HOOCCH_2)_2NH \xrightarrow{N_2O_3;\ H_2O} (HOOCCH_2)_2N{-}NO\ .$$

The dinitrile and the dimethyl esters of nitrosiminodiacetic acid were obtained with nearly quantitative yields in ether [94].

Brookes and Walker [95], who allowed nitrogen trioxide to react with α-aminoacetonitriles, observed that the former is not only a nitrosating agent but also promotes the cyclisation of the intermediate *N*-nitrosoacetonitriles to sydnoneimines:



Despite the fact that the method of introduction of the nitroso-group with the aid of nitrogen trioxide gives as a rule good results, it has not found as wide an application as "acid" nitrosation. This is probably because the process is complicated by the necessity to obtain nitrogen trioxide. The latter is usually obtained from sodium nitrite and sulphuric acid [95] or by the reaction of nitric acid with arsenic oxides [94].

Above its boiling point nitrogen trioxide readily decomposes into NO and NO_2. This property constitutes the basis of the synthesis of nitrosamines. Thus *N*-chlorodialkylamines are readily converted into *N*-nitrosodialkylamines when acted upon by nitric oxide in solutions containing the redox system Fe^{3+}/Fe^{2+} or Cu^{2+}/Cu^{+}. [96] Similarly *N*-nitrosodi(trifluoromethyl)amine was synthesised from *N*-bromodi(trifluoromethyl)amine [97]. A radical mechanism was proposed for the reaction:

$$R_2N{-}Hal \rightarrow R_2N^{\cdot} + Hal^{\cdot},$$
$$Hal^{\cdot} + NO \rightarrow \dot{N}O,$$
$$R_2N^{\cdot} + \dot{N}O \rightarrow R_2N{-}NO\ .$$

The gas-phase or liquid-phase nitrosation of secondary alkylamines probably takes place by a radical mechanism [98,99]. The reaction is performed in an autoclave at a high temperature, after mixing nitrogen oxides and the amine. Judging from patent data, *N*-nitrosodialkylamines are formed when nitric oxide reacts with secondary amines under pressure in the presence of transition metal salts, metallic nickel, palladium, or rhodium [100]. *N*-nitrosodiethylamine is formed when the adduct of diethylamine with nitric oxide is decomposed in the presence of oxygen [101]. The kinetics of the reaction of diethylamine with nitric oxide have been investigated. The reaction is of first order with respect to diethylamine and proceeds via the intermediate adduct $(C_2H_5)_2NH.N_2O_2$, which reacts with a second molecule of nitric oxide and then with diethylamine. The activation energy for the reaction is 12 kcal mole^{-1}. [102]

The use of nitrogen tetroxide and nitrosyl chloride as nitrosating agents has been insufficiently investigated although they have been known for a long time and are used for the nitrosation of amines and amides [16,89,103]:

$$[(NO_2)_3CCH_2]_2NH + N_2O_4 \xrightarrow{CH_3COOH+CH_3COOK} [(NO_2)_3CCH_2]_2N{-}NO + HNO_3\ ,$$
$$Et_2NH_2 \cdot NO_3 + NO \cdot NO_3 \rightarrow Et_2N{-}NO + 2HNO_3\ .$$

The reaction of nitrosyl chloride with secondary amines was investigated by Solonina [104]. When nitrosyl chloride was passed into a solution of the amine in ether, *N*-nitroso derivatives of dipropyl-, di-isobutyl-, and dipentyl-amines were synthesised. Later it was shown that the reaction of nitrosyl chloride with diethylamine hydrochloride results in a quantitative yield of the *N*-nitroso-derivative:

$$Et_2NH_2 \cdot Cl + NOCl \rightarrow Et_2N{-}NO + 2HCl\ .$$

The synthesis of *N*-nitroso-di-t-butylamine in 23% yield from di-t-butylamine and nitrosyl chloride has been described [105].

3. Cleavage of Tertiary Amines Accompanied by Nitrosation. Syntheses of Nitrosamines from Primary Amines

Until recently there has been no unanimous view on the cleavage of tertiary amines with nitrous acid. Not until 1967 was it shown convincingly that tertiary amines can be converted into nitrosamines by nitrous acid [106], although examples of this reaction were known in the past century. Geuther [107] obtained *N*-nitrosodiethylamine from triethylamine, but Heintz [108] was unable to reproduce his results and arrived at the erroneous conclusion that tertiary amines do not react with nitrous acid. This initiated the controversy which continued for more than one hundred years. Subsequently the validity of Geuther's results was confirmed by Solonina [109], who investigated the cleavage of forty nitrite salts of amines and in all cases observed the formation of nitrosamines, and also by other investigators [110-112]. The cleavage of tertiary amines by nitrous acid is discussed in detail in the literature [106,112].

The most probable mechanism of the cleavage includes attack by the nitrosating agent on the free electron pair of the nitrogen atom and the formation of the nitrosimmonium ion. The latter splits off the "nitroxyl" (HNO) and hydrolyses under the reaction conditions to a secondary amine. A ketone or an aldehyde is formed as a side product [106]:

$$R_2N{-}CHR_2' \xrightarrow{HNO_2} R_2\overset{+}{N}\!\!<^{CHR_2'}_{NO} \rightarrow R_2\overset{+}{N}{=}CR_2' + HNO\ ,$$
$$R_2\overset{+}{N}{=}CR_2' \xrightarrow{H_2O} R_2'C{=}O + R_2\overset{+}{N}H_2 \xrightarrow{HNO_2} R_2N{-}NO\ ,$$
$$2HNO \rightarrow H_2N_2O_2 \rightarrow H_2O + N_2O\ .$$

The degree of conversion of the tertiary amine into the nitrosamine reaches 50–70%.

The cleavage of tertiary amines with nitrous acid and nitrosyl chloride has been described [103]. Thus, on refluxing in alcohol with nitrous acid, tribenzylamine is smoothly converted into *N*-nitrosodibenzylamine and benzaldehyde.

The results obtained with nitrosyl chloride are contradictory. In an early study Solonina noted that tri-isobutylamine is cleaved with nitrosyl chloride to *N*-nitrosodi-isobutylamine [104]. According to these data [114], when cyclohexyldimethyl- and dicyclohexylmethyl-amines are acted upon by nitrosyl chloride, *N*-nitrosocyclohexylmethyl- and *N*-nitrosodicyclohexyl-amines are formed respectively. In another publication [115] it was noted that the reaction of trimethylamine with nitrosyl chloride gives only the hydrochlorides of di- and tri-methylamines: the reaction with tribenzylamine results in the formation of the hydrochlorides of tribenzylamine and dibenzylamine and of benzaldehyde [106]. The same products are formed in the reaction of tribenzylamine with nitrosonium tetrafluoroborate [106]. Probably the basicity of the nitrogen atom is important for the cleavage of tertiary amines to the corresponding *N*-nitroso-compounds. For example, triglycineamine, the basicity of the nitrogen atom in which is reduced, is incapable of undergoing cleavage with nitrosation [116]. Diethylaminotrimethylsilane is readily cleaved by nitrosyl chloride [117]:

$$(C_2H_5)_2NSi(CH_3)_3 + NOCl \rightarrow (C_2H_5)_2N{-}NO + (CH_3)_3SiCl .$$

In 1920 a method for the preparation of *N*-nitrosodialkylamines by the cleavage of tertiary amines with tetranitromethane was discovered. The reaction takes place when alcoholic solutions of tertiary amines are heated with tetranitromethane in the presence of pyridine [118]:

$$R_1R_2NCH_2R + C_5H_5N + C(NO_2)_4 \rightarrow R_1R_2N{-}NO + RCHO + C_5H_5N \cdot HC(NO_2)_3 .$$

A large series of *N*-nitrosodiaryl-, *N*-nitrosoarylalkyl-, and *N*-nitrosodialkyl-amines was synthesised by this procedure. Subsequently a similar cleavage was achieved in the absence of pyridine in acetic acid [119]. Nitroform is formed as a side product.

In connection with the nitrosating activity of tetranitromethane, it is interesting to note that this compound exhibits nitrosating and nitrating properties in relation to aromatic compounds [120-122], a nitro-group can be replaced by a halogen [123,124] or an alkyl residue in polar aprotic solvents [125], and is tetranitromethane capable of a number of other extremely interesting reactions [126-128].

Cleavage of tertiary amines accompanied by nitrosation takes place also under the action of bromonitroform in chloroform. This is accompanied by the bromination and nitration of the benzene ring. Thus the reaction of bromotrinitromethane with dimethylaniline leads to the formation of *N*-methyl-*N*-nitroso-*p*-bromoaniline and *NN*-dimethyl-*p*-nitroaniline [129].

In his study of the reaction of silver nitrite with the hydrochlorides of n-propyl- and n-butyl-amines, Meyer observed that, together with other products, low yields of *N*-nitrosodipropyl- and *N*-nitrosodibutyl-amines are formed in this process [130,131]. Deamination of n-propylamine gave a mixture of propanol, 2-propanol, and *N*-nitrosodipropylamine [132].

Under thermolysis conditions, the nitrite salts of methyl- and ethyl-amines tend to undergo similar reactions [18].

When ethyl- and isobutyl-amines were treated with nitrosyl chloride in ether, *N*-nitrosodiethyl- and *N*-nitrosodi-isobutyl-amines were formed together with corresponding alkyl chlorides. It is interesting that the author explained "their formation (nitrosamines) via the preliminary synthesis of secondary amines by the action of the alkyl chlorides on the primary amines". Seconday amines are then converted into nitroso-compounds [133].

Although the method of preparation of the nitrosamines from primary amines has no preparative importance, it is interesting from the theoretical standpoint. Since the mechanism of the denitrosation of amines is presumed to involve the formation of an intermediate carbonium ion [11], the results described above can be accounted for by the alkylation of the primary amine by the carbonium ion:

$$RNH_2 \xrightarrow{HNO_2} R{-}N{=}N{-}OH \xrightarrow{H^+} R^+ ,$$

$$RNH_2 + R^+ \rightarrow \underset{\displaystyle R}{\overset{\displaystyle +}{R}}NH_2 \xrightarrow[-H_2O]{HNO_2} R_2N{-}NO .$$

Cleavage of amines accompanied by nitrosation is of preparative interest as a method for the purification of secondary amines. Thus, when a mixture of primary, secondary, and tertiary amines is treated in succession with a nitrosating agent and potassium permanganate, only the *N*-nitrosodialkyl-amine remains [134]. A method for the synthesis of pure *N*-nitrosodialkylamines by the nitrosation of a mixture of di- and trialkylamines has also been described [104,110].

4. Other Methods

The preparation of *N*-nitrosodipropylamine from the nitrite salt of dipropylamine by fusing the latter or heating it in water has been described [135]. *N*-Nitrosodimethyl- and *N*-nitrosodiethyl-amines are formed when nitrite [18] and nitrate salts of dimethyl- and diethyl-amines are heated [136], via the following mechanism:

$$(CH_3)_2NH \cdot HNO_3 \xrightarrow{\Delta} (CH_3)_2NH \cdot HONO \rightarrow (CH_3)_2N{-}NO + H_2O + O .$$

N-Nitrosodibenzylamine was isolated when tetrabenzylhydrazine [137] and *NN*-dibenzylhydroxylamine were treated with nitric acid [35]:

$$(C_6H_5CH_2)_2N{-}X \xrightarrow{HNO_2} (C_6H_5CH_2)_2N{-}NO;\ X{=}OH;\ N(CH_2C_6H_5)_2 ,$$

It has been reported that *N*-nitrosodibenzylamine is formed when isopentyl nitrite reacts with dibenzylamine [138]. Titov employed benzyl nitrite to nitrosate diethylamine [139]; a continuous method for the synthesis of *N*-nitrosodimethylamine with a yield in excess of 90% by the nitrosation of dimethylamine in alcohol with methyl nitrite has been described [140].

The formation of *N*-nitrosodi-isopropyl-, *N*-nitrosodibutyl-, and *N*-nitrosodi-(β-nitroxyethyl)amines has been observed in the catalytic nitration of the corresponding amines in the presence of zinc chloride [27,141]. In this connection, one may note that the catalytic effect of Cu^{2+} ions in the nitrosation of diethylamine in methanol with nitric oxide under pressure has also been investigated [142,143]. The effects of temperature, pressure, and the concentration of nitrogen oxides on the mode of reaction have been studied. The optimum yield of *N*-nitrosodiethyl-amine (93.8%) is attained in the reaction carried out at 30°C at a pressure of 1 atm. The reduction of temperature to −30°C, an increase of pressure, and an increase of the concentration of nitric oxide leads to a fall of the yield of the nitrosamine to 11–15% owing to the formation of methyl nitrite. The nitrosating species is $CuNO^{2+}$. The kinetics of the reactions were investigated.

According to patent data, when 1,1,1,6-tetranitro-3,6-diazaheptane is nitrated with a mixture of acetic anhydride and nitric acid, 1,1,1,6-tetranitro-3-nitroso-3,6-diazaheptane is formed [144]. We believe that this result is most probably "fortuituous". It is likely that the authors employed nitric acid containing a high content of nitrogen oxides, which were in fact responsible for the nitrosation of the amine.

Nitration of a ternary mixture of ammonium chloride, the ammonium salts of nitroform and di-(2,2,2-trinitroethyl)amine, formed in the condensation of methylenediamine hydrochloride with 2,2,2-trinitroethanol, and nitric acid in acetic anhydride leads to the formation of *N*-nitrosodi-(2,2,2-trinitroethyl)amine with an admixture of the nitramine [89]. The authors attribute the appearance of the *N*-nitroso-derivative to the catalytic effect of the chloride ions. The capacity of a mixture of acetic anhydride and nitric acid to behave as a nitrosating agent was noted by Wright and coworkers [27]. However, the nitrosation of di-(2,2,2-trinitroethyl)amine in this mixture can also take place in the absence of chloride ions under the action of N_2O_4.

The formation of *N*-nitrosodi-(2,2,2-trinitroethyl)amine was observed in the condensation of 2,2,2-trinitroethanol with hydroxylamine and also in the reaction of nitroform with formaldoxime in the presence of sulphuric acid [89]. The mechanism of the reaction was not established:

$$2\,HC(NO_2)_3 + 2\,CH_2{=}NOH \xrightarrow{H_2SO_4} [(NO_2)_3CCH_2]_2N\text{-}NO.$$

IV. PHYSICAL PROPERTIES, STRUCTURE, AND SPECTRA

1. General Characteristics

In the wide class of *N*-nitrosodialkylamines, the properties of the simplest members (*N*-nitrosodimethyl- and *N*-nitrosodiethyl-amines) were most fully investigated. The lower *N*-nitrosodialkylamines are yellow or yellow-green non-hygroscopic liquids, which are partially soluble in water and readily soluble in organic solvents. Their boiling points increase with the increasing size of the alkyl substituents and lie in the range 150–220°C. As a rule, substituted nitrosamines are yellow crystalline compounds. In this connection, it is important to note that *N*-nitrosopolynitroalkylamines are colourless, which is undoubtedly due to the effect of the polynitroalkyl substituents on the $p-\pi$ conjugation in the nitrosamines. Compared with the related nitramines, *N*-nitrosodialkylamines have lower boiling and melting points. The densities of the majority of nitrosamines are relatively low and lie in the range 0.9–1.2 g cm^{-3}, increasing with the molecular weight.

The dipole moments of *N*-nitrosodialkylamines are evidence of a considerable polarity of the molecules. For example, the dipole moment of *N*-nitrosodimethylamine is 3.98 D, [145] while that of *N*-nitrosodibutylamine is 4.32 D. [146] The introduction of electron-accepting substituents into the molecule leads to a decrease of the dipole moment. Thus the dipole moment of *N*-nitroso-*N*-phenylaminoacetic acid is 3.18 D [147] and those of *N*-nitrosomethylaniline and *N*-nitrosodiphenylamine are 3.62 and 3.39 D respectively [148]. The replacement of each methyl group by a phenyl group leads to a decrease of the dipole moment of the nitrosamine by 0.3 D. [148] Therefore we believe that it is of interest to investigate the dipole moments of nitrosamines with other electronegative substituents such as trifluoro-, trichloro-, and trinitromethyl groups, which will make it possible to trace their effect on the conjugation in the nitrosamino-group by the dipole moment method.

The average refraction of the N–N bond in *N*-nitrosodialkyl-amines hardly differs from the value in asymmetric dialkyl-hydrazines and amounts to 1.99. The refraction of the >N–N=O fragment is 7.748 and slightly exceeds the group refraction in dialkylhydrazines [54,149]. The parachors of the N=O and >N–N=O groups in a number of *N*-nitrosodialkylamines have been determined and the average values of these quantities have been found to be 53.4 and 68.0 respectively [54,149].

The literature quotes certain thermochemical parameters for *N*-nitrosodimethylamine: heat of combustion (382 ± 1.5 kcal $mole^{-1}$), heat of formation in the standard state (−10.7 ± 1.5 kcal $mole^{-1}$), heat of evaporation (9.9 ± 0.5 kcal $mole^{-1}$), and heat of formation in the gas phase (−0.8 ± 2 kcal $mole^{-1}$). [150]

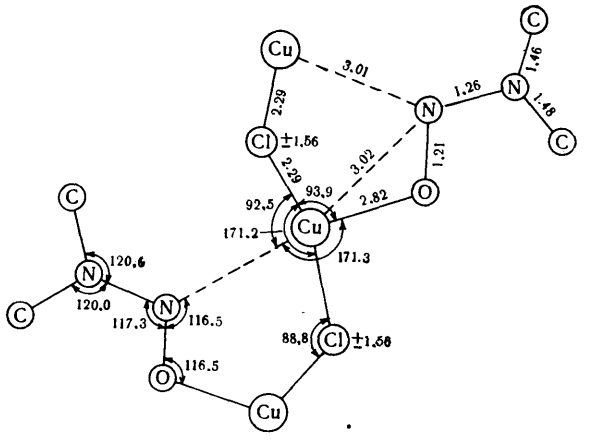
The dissociation energy of the N–N bond in *N*-nitrosodimethylamine, determined by the electron impact method, is 43 kcal $mole^{-1}$, [151] while according to other data it is 32 kcal $mole^{-1}$. [152] This quantity was recently estimated more accurately in a study already quoted [150] and was found to be 55.2 kcal $mole^{-1}$. Thus, contrary to earlier data, the N–N bond in *N*-nitrosodimethylamine proved to be stronger than in *N*-nitro-di-methylamine to the extent of 14.1 ± 5.2 kcal $mole^{-1}$ according to thermochemical data and 11.3 ± 3.0 kcal $mole^{-1}$ according to kinetic data [150]. These data appear to be the most correct, since they are consistent with the hypothesis of $p-\pi$ conjugation in the nitrosamine group, as a result of which the amount of N–N multiple bond character in nitrosamines is enhanced (about 49%) compared with that in nitramines (about 15%). [153–155]

2. Structure and Spectra

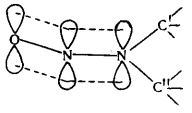
The molecules of aliphatic nitrosamines have coplanar structures in the gaseous and crystalline states. Both nitrogen atoms are in the state of sp^2 hybridisation, which is confirmed by the C′–N–N (120.3°), C″–N–N (116.4°), and N–N–O (113.6°) valence angles in *N*-nitrosodimethylamine. The bond lengths in *N*-nitrosodimethylamine are as follows: 1.235 Å for N–O, 1.344 Å for N–N, 1.461 Å for C–N, and 1.129 Å for C–H. It is interesting that the N–N bond in *N*-nitrosodimethylamine is shorter by 0.04 Å than in *N*-nitrodimethylamine, which has been attributed to the greater electron-accepting activity of the nitroso-group compared with the nitro-group [156]. The N–N bond length in *N*-nitrosodimethylamine agrees well with its enhanced multiplicity and strength compared with those in *N*-nitrodi-methylamine.

The planar disposition of the nitrosoamino-group has been established by an X-ray diffraction study of the adduct of *N*-nitrosodimethylamine with copper chloride. The bond between the copper atom and the nitrosamine is formed via the oxygen atom of the nitroso-group. The nitrogen atom of the nitroso-group is located at equal distances from the neighbouring copper atoms. The considerable difference between the Cu–O and Cu–N distances may be due to the fact that the copper atom is displaced by 0.2 Å from the plane passing through the chlorine atoms [157]. The shortening of the N–N bond in the complex compared with the free nitrosamine can be

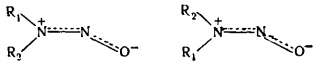
accounted for by the transfer of electron density from the dimethylamino-group to the nitroso-group [156]:



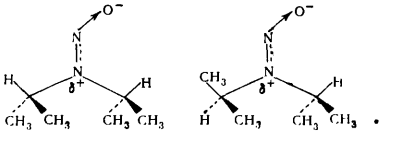
The disposition of the atoms in the nitrosamino-group in one plane naturally facilitates the overlapping of the *p* orbital of the amino-nitrogen atom with the π-electron cloud of the N⋯O bond. The force constant of the N⋯O bond in nitrosamines is 6.8 mdyn Å^{-1}. [158] According to this value, the multiplicity of the N⋯O bond in nitrosamines is between 1 and 1.5:



In a number of studies the internal rotation about the N–N bond with partial double bond character was investigated. The barrier to rotation about this bond is estimated as approximately 24 kcal mole^{-1}. [159–161] This leads to the appearance of *s-cis-trans* isomerism in nitrosamines. The presence of the isomers of a large number of *N*-nitroso-derivatives has been demonstrated by NMR spectroscopy [162,163]:



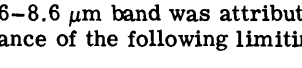
Only the *cis*-methyl isomer has been detected for *N*-nitrosomethylphenylamine. Both isomers have been found for *N*-nitrosoethylphenylamine and *N*-nitrosoisopropylphenylamine. The conformations of the alkyl substituents in *N*-nitrosoisopropylmethyl-, *N*-nitroso-t-butylmethyl-, and *N*-nitrosodi-isopropyl-amines are discussed in the same paper. The following conformations are characteristic of *N*-nitrosodi-isopropylamine:



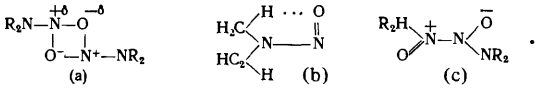
ΔH for the *cis–trans* isomerisation of *N*-nitrosobenzylmethyl-amine is less than 1 kcal mole^{-1}. [158] The *cis-trans* isomers of benzyl-2,6-dimethyl-*N*-nitrosoanilines were separated by thin-layer chromatography. The bulky 2,6-dimethylphenyl group evidently stabilises the isomers. Both substances are stable in the crystalline state [162]. Rotational isomerism has also been observed for *N*-nitrosobenzylisopropylamine [164,165]. The equilibrium mixture of the isomers was separated into its components by crystallisation from carbon disulphide [165]. The ratios of the areas of proton signals for certain *cis*- and *trans*-isomers have been investigated as a function of the bulk of the alkyl substituents. The screening of the protons of the *cis*-isomers is more pronounced than that of the protons of the *trans*-isomers, owing to the diamagnetic anisotropy of the N=O bond [166].

In a study of the optical rotatory dispersion it was observed that an intense cotton effect is characteristic of various nitrosamines in the range 350–400 nm. [167] The $n-\pi^*$ and $\pi-\pi^*$ transitions are active in the nitroso-chromophores [168–171]. For example, in aqueous solution of *N*-nitrosodimethylamine the $\pi-\pi^*$ transition is shown in the region of 228 nm and the $n-\pi^*$ transition in the region of 332 nm. [169] The studies on the optical circular dichroism of nitrosamines have been reviewed in a monograph [172]. The sector rule for nitrosamines and its correlation with the stereochemistry of these compounds have been described [161].

Although a large number of infrared spectra of nitrosamines have been described in the literature, few systematic accounts of the assignments of the absorption frequencies are available [77,159,173–180]. In one of the first detailed studies of the infrared spectroscopy of nitrosamines, Haszeldine and Jander [174] drew attention to the inconsistency between the absorption bands of the N=O bond in nitrosamines and those for nitramines, nitrites, and *C*-nitroso-compounds. They observed in the infrared spectra of nitrosamines three relatively intense bands in the region of 7.1–7.4, 7.6–8.6, and 9.15–9.55 μm. The first two were assigned to the vibrations of the N=O bond and the last to the vibrations of the N–N bond. The appearance of the 7.6–8.6 μm band was attributed by the authors to the resonance of the following limiting structures:



To confirm these conclusions, a study was made of the effect of various solvents and the state of aggregation on the nature of the spectral changes [77,175]. It was found that the spectra of nitrosamines in the liquid state differ from those recorded in solvents (carbon tetrachloride and chloroform), particularly in the range of frequencies characteristic of the N=O bond. The authors attribute these changes to three causes: (a) dipole–dipole interaction between molecules, (b) intramolecular binding of the alkyl hydrogen by the oxygen atom of the nitroso-group, and (c) dimerisation of the molecules:



The predominance of a particular type of interaction depends on the conditions under which the nitrosamine exists. In the gaseous states the molecules are of course not associated and therefore the N=O absorption band is closer to that in the spectra of nitramines. In the liquid state monomer–dimer equilibrium obtains and the N=O absorption band is displaced towards longer wavelengths (6.74 and 6.93 μm respectively for *N*-nitrosodiethylamine).

Polar solvents have a similar effect. The N–N absorption band varies in exactly the same way. For example, in the spectrum of gaseous *N*-nitrosodiethylamine it is in the region of 9.55 μm and in that of the liquid substance it is displaced to 9.35 μm. The idea of a monomer–dimer equilibrium in nitrosamines was supported by Tarte [176] and by Piskorz and Urbański [177].

An interesting observation was made in a study of the infrared spectrum of *N*-nitrosodi-(2,2,2-trifluoroethyl)-amine, one of the few *N*-nitroso-derivatives containing electron-accepting substituents [77]. In this substance the N=O absorption bands are displaced under the influence of the trifluoroalkyl groups towards shorter wavelengths and are located in the region of 6.45 μm for the gaseous nitrosamine and in the region of 6.60 μm for the liquid substance. The displacement of the bands was attributed by the authors to a decrease of the polarity of the *N*-nitrosodi-(2,2,2-trifluoroethyl)amine molecule, which reduces sharply the interaction between the individual molecules. It is interesting that the N–N bond vibration frequencies in *N*-nitrosodi-(2,2,2-trifluoroethyl)amine in solution, or following a change in the state of aggregation, are displaced less than for unsubstituted nitrosamines.

Williams et al. [178], who postulated the occurrence of mesomerism in nitrosamines, suggested that, when the spectra are recorded in polar solvents, the absorption bands associated with the N=O bond vibrations (6.6–6.7 μm) should be displaced towards longer wavelengths. On the other hand, the N–N absorption band should be shown at lower wavelengths. This hypothesis was confirmed experimentally. In the spectra of *N*-nitrosodimethylamine in carbon tetrachloride and methylene bromide $\lambda_{N=O}$ is 6.85 and 6.94 μm, the corresponding values for the N–N absorption band (λ_{N-N}) being 9.66 and 9.52 μm. An analogous situation was found in the spectra of other nitrosamines.

The wavelength corresponding to the N=O bond in the nitrosamines is much higher than for *C*-nitroso-derivatives which can be accounted for by the greater contribution to the structure of nitrosamines of the canonical form (II). [178] The hypothesis of the dimerisation of nitrosamines put forward by Haszeldine and coworkers was rejected by Williams [178] and other investigators [171,179,180].

The Table summarises the principal literature data on the infrared spectra of nitrosamines.

Comparison of the infrared spectra of *N*-nitrosodi-(2,2,2-trifluoroethyl)amine with those of unsubstituted analogues demonstrates that electron-accepting substituents have a significant influence on the structure of the nitrosamino-group, probably by reducing the degree of p-π conjugation. This conclusion has been confirmed experimentally in a study of the chemical properties of *N*-nitrosopolynitroalkylamines. It is significant that in the infrared spectrum of *N*-nitrosodi-(2-bromo-2,2-dinitroethyl)amine and *N*-nitrosodi-(2,2,2-trinitroethyl)amine, bands with ν_{NO} = 1490 and 1520 cm^{-1} and ν_{N-N} = 980 and 1020 cm^{-1} respectively are characteristic of the nitrosamino-group†.

In the ultraviolet spectra of nitrosamines there are two absorption bands in the region of 235 and 365 nm, [174] 230 and 374 nm, [177] 230 and 365 nm, [77] and 228 and 332 nm [169] (in water). The first of these is more distinct than the second. The bands were assigned by comparing the spectra of nitrosamines with those of nitrites and nitramines. In the ultraviolet spectra of nitramines, there is a strong absorption in the region close to 235 nm and in the spectra of nitrites in the region of 375 to 380 nm. [77,175] Therefore the absorption band in the region of 230–235 nm in the spectra of nitrosamines characterises the N–N bond and the absorption in the region of longer wavelengths is due to the N=O bond [175].

The positions of the bands in the ultraviolet as well as infrared spectra, depend greatly on the nature of the solvent. For example, on passing from a non-polar solvent to water, the 365 nm band is displaced to 331 nm. This shows that the N=O bond is sensitive to external effects. A similar observation was made in a study of the ultraviolet spectrum of *N*-nitrosodi-(2,2,2-trinitroethyl)amine [89].

Infrared spectra of certain nitrosamines R_2N-NO.

R	Liquid		Soln. in CCl_4		Пар	
	$\nu_{N=O}$, cm^{-1}	ν_{N-N}, cm^{-1}	$\nu_{N=O}$, cm^{-1}	ν_{N-N}, cm^{-1}	$\nu_{N=O}$, cm^{-1}	ν_{N-N}, cm^{-1}
CH_3	1445	1048	1460	1041	1488	1015
C_2H_5	1448	1069	1459	1061	1485	1048
$n\text{-}C_3H_7$	1455	1069	1460	1067	1486	1049
$iso\text{-}C_3H_7$	—	—	1438	1139	—	—
$s\text{-}C_4H_9$	—	—	1437	1135	—	—
$n\text{-}C_5H_{11}$	1460	1084	—	1082	—	—
$C_6H_5CH_2$	—	—	1463	1120	—	—
C_6H_{13}	1460	1090	—	1085	—	—
F_3CCH_2	1515	1052	1528	1046	1550	1046

Electron-accepting substituents have an appreciable effect on the absorption by the nitroso-group. Whereas the absorption by the N=O bond in *N*-nitrosodiethylamine occurs in the region of 360 nm, in the *N*-nitroso-derivatives of di-(2,2,2-trinitroethyl)-, di-(2-bromo-2,2-dinitroethyl)-, and di-(2,2,2-trifluoroethyl)amines it is displaced to the region of 380 nm. Information about these effects of the nature of the substituent on the >N–N=O fragment is also provided by mass spectrometric data. For example, *N*-nitrosodimethylamine dissociates with formation of $C_2H_4N^+$ as the major ion (19.2%), while *N*-nitroso-di(trifluoromethyl)amine gives the CF_3^+ major ion (37.8%). [181]

V. CHEMICAL PROPERTIES

Aliphatic nitrosamines are highly reactive. The reason for their reactivity is that the nitrosamino-group has four lone pairs of electrons, which make nitrosamines potential Lewis bases. The occurrence of p-π conjugations with the withdrawal of the electron cloud towards the oxygen atom is responsible for many interesting reactions of nitrosamines. In the first place these are the complex-formation reactions, reaction with inorganic acids, reduction to *NN*-substituted hydrazines, oxidation and nitration, cyclisation to sydnones, and sydnoneimines, and photochemical reactions.

†The absorption frequencies were assigned by the authors of the review on the basis of the spectra quoted by Grimes et al. [89]

2. Reaction with Inorganic Acids, Hydrogen Bonds, and Complex-formation Capacity of Nitrosamines

When inorganic acids act upon nitrosamines, the nitroso-group is split off with formation of amine salts. In one of the first studies [6] it was already noted that, when hydrogen chloride is passed into an emulsion of *N*-nitrosodiethylamine in water, the nitroso-derivative rapidly dissolves. When an ethereal solution of *N*-nitrosodiethylamine is treated with hydrogen chloride, a salt with the composition $(C_2H_5)_2NNO.HCl$ is formed, and then readily decomposes on addition of water or alcohol [52].

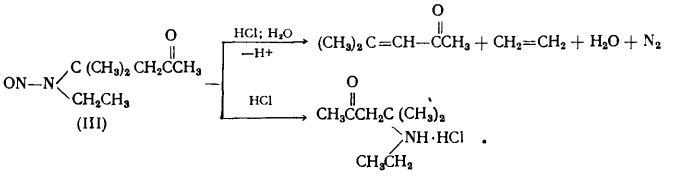
N-Nitrosodimethylamine decomposes on heating with hydrochloric acid into dimethylamine hydrochloride and nitrous acid. Hydrochloric acid acts similarly on *N*-nitrosodibutylamine [31], *N*-nitrosomethylallylamine [82], *N*-nitrosodibenzylamine, and others [43,55,182]:

$$R_1R_2N{-}NO \xrightarrow{HCl;\ H_2O} R_1R_2NH \cdot HCl + HNO_2 .$$

Hydrogen chloride has a more pronounced denitrosating activity [6,42,113,134]. Some investigators have also proposed a method for the preparation of pure secondary amines involving the treatment of nitrosamine solutions in ether or toluene with hydrogen chloride [42,134].

It is interesting that the denitrosation takes place more readily than the hydrolysis of the nitrile group. Thus, in an attempt to hydrolyse the dinitrile of *N*-nitrosiminodiacetic acid, Curtius [94] isolated as the main product the hydrochloride of the dinitrile of iminodiacetic acid.

The carbonyl group has a significant influence on the result of the denitrosation. When the nitroso-derivative (III) is treated with hydrochloric acid, ethylene and mesityl oxide are formed [41]. In contrast to hydrochloric acid, hydrogen chloride has only a denitrosating effect:



It has been noted that, when *N*-nitrosopolynitroalkylamines are denitrosated, it is impossible to isolate the salts of polynitroalkylamines or the free amines. Evidently in this case a more profound degradation of the molecule takes place, owing to the reduced basicity of the amino-nitrogen in polynitroalkylamines [89,183].

Apart from hydrochloric acid and hydrogen chloride, bromine and sulphuric acid have been used as denitrosating agents [113,184]:

$$(C_6H_5CH_2)_2N{-}NO \xrightarrow[-NO]{Br_2} (BrC_6H_4CH_2)_2NH \cdot HBr .$$

The study of the kinetics of the cleavage of aliphatic nitrosamines by acids led to the hypothesis that the splitting off of the nitroso-group is preceded by the occurrence of an equilibrium between the nitrosamine and its protonated form. The protonated nitrosamine then splits off the nitroso-group in the form of the nitrosonium cation and is itself converted into the corresponding amine:

$$R'RN{-}N{=}O + H^+ \leftrightarrows R'R\overset{+}{N}H{-}N{=}O ,$$
$$R'R\overset{+}{N}H{-}N{=}O \rightarrow R'RNH + \overset{+}{N}O \ (\text{slow}) .$$

The hydrolysis is easier the more electrophilic is the R or R′ group. In hydrochloric acid the denitrosation takes place more readily than in sulphuric or perchloric acid. The authors explain this by the nucleophilic reaction

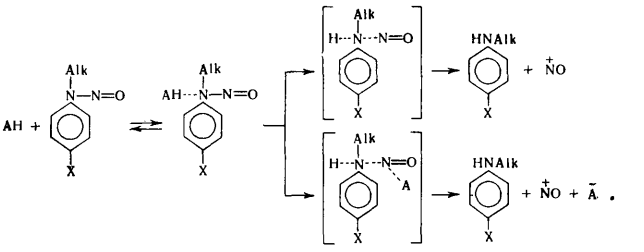
$$\overset{+}{N}H{-}N{=}O \xrightarrow{Cl^-} \overset{+}{N}H{-}N\begin{matrix}Cl\\O^-\end{matrix} \rightarrow NH + NOCl .$$

The rate of hydrolysis obeys the Hammett equation [185,186]:

$$\lg K + H_0 = \text{const.}$$

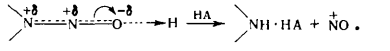
According to the data of Porai-Koshits and coworkers [187–190], the denitrosation of aliphatic-aromatic nitrosamines takes place by a "push–pull" mechanism. Preliminary protonation of the nitrosamino-group was not observed. The splitting off of the nitroso-group is promoted by the additional polarisation of the N–N bond owing to the formation of a hydrogen bond involving the nitrogen atom of the amino-group. The formation of the new N–H bond takes place simultaneously with the splitting off of the nitroso-group.

The presence of electron-accepting substituents in the *para*-position of the aromatic ring lowers the basicity of the amino-nitrogen in the nitroso-derivative and in this case the nucleophilic attack by the acid anions plays a decisive role. However, acid anions participate in the splitting off of the nitroso-groups only in the presence of hydrogen ions. On the basis of the results obtained, the following reaction mechanisms have been proposed as a function of the structure of the nitrosamine:

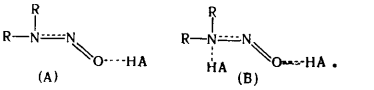


The results of studies on the formation of hydrogen bonds in aliphatic nitrosamines and also their chemical behaviour show that the reaction centre is located at the oxygen atom of the nitroso-group, which is inconsistent with the above hypothesis concerning the denitrosation of nitrosamines.

We believe that a more correct mechanism of the denitrosation of aliphatic nitrosamines involves electrophilic attack on the oxygen atom of the nitroso-group. The latter is readily eliminated as a result of the generation of partial positive charges at the nitrogen atom [157]:



The reaction of nitrosamines with trichloroacetic acid in cyclohexane takes place with formation of one or two hydrogen bonds and may be described by the following structures [168]:



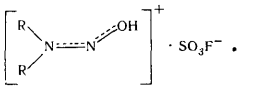
A number of changes takes place in the ultraviolet spectrum of *N*-nitrosodimethylamine in aqueous sulphuric acid solution due to acid–base interaction [169]:

$$R_2NNO \ldots (H_2O)_x \overset{H_2SO_4}{\rightleftharpoons} R_2NNO \ldots (H_2O)_x H_2SO_4 ,$$
$$R_2NNO \ldots (H_2O)_x \leftrightarrows R_2NNO \ldots (H_2O)_x HSO_4^- ,$$
$$R_2NNO \ldots (H_2O)_x HSO_4^- \rightleftarrows R_2NNOH^+ \ldots (H_2O)_x ,$$
$$R_2NNO \ldots (H_2O)_x HSO_4^- \leftrightarrows R_2NNO \ldots (H_2O)_x (H_2SO_4)_2 ,$$
$$R_2NNO \ldots (H_2O)_x HSO_4^- \rightleftarrows R_2NNO \ldots (H_2O)_x (HSO_4)_2 .$$

The attempts to isolate the salts of the nitrosamine and sulphuric acid were unsuccessful, but unstable white 1 : 1 crystalline adducts of 72% perchloric acid with *N*-nitroso-di-n-heptylamine, *N*-nitrosodi-n-octylamine, and *N*-nitrosodi-(2-ethylhexyl)amine were obtained, which indicates the possibility of proton transfer to the oxygen atom of the nitroso-group.

Nitrosamines form hydrogen bonds with formic, acetic, and trifluoroacetic acids and with alcohols, phenols, and amines [171 191-193]. The proton-donating activity of alcohols in the formation of the hydrogen bond increases in the series primary > secondary > tertiary. The equilibrium constants for the hydrogen-bonded complexes of nitrosamines and phenols increase linearly with the pK_a of the phenols [191].

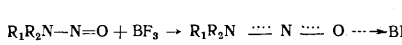
A detailed study of the protonation of *N*-nitrosodimethyl- and *N*-nitrosodiethylamines and also *N*-nitrosopiperidine by NMR spectroscopy was undertaken [194]. The characteristic signal associated with the interaction of the proton with the nitrosamine occurs only in fluorosulphonic acid at 0°C and below. In other acids the spectra also show changes characteristic of structure (A); the dialkylamino-group is not protonated. The spectra shows that the formation of the hydrogen bond or protonation involves the oxygen atom of the nitrosamino-group. A structure with a delocalised positive charge has been proposed for the adducts of nitrosamines with fluorosulphonic acid:



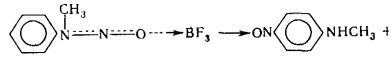
The delocalisation of the positive charge probably prevents further protonation of the molecule.

A study of the competing protonation of *N*-nitrosodimethylamine and dimethylformamide by trifluoroacetic acid in 2-nitropropane showed that the nitrosamine is a weaker base [194].

The basic nature of the oxygen atom is shown by the capacity of nitrosamines to give rise to brightly coloured stable complexes with bromoplatinic acid, the composition of which corresponds to the formula $[R_2NNO.H]_2PtBr_6$. [195] Complexes of nitrosamines with boron trifluoride are formed when equimolar amounts of the nitrosamine and boron trifluoride-ether are mixed or when an ethereal solution of the nitrosamine is treated with boron trifluoride [196]:



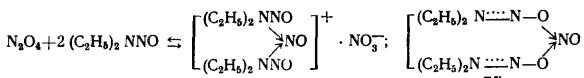
The stability of the complexes increases with the electron-donating capacity of the substituent linked to the nitrogen atom. The complex with *N*-nitrosodiphenylamine could not be isolated. It is interesting that in the adduct of boron trifluoride and *N*-methyl-*N*-nitrosoaniline the N–N bond is so much weakened that rapid rearrangement to *N*-methyl-*p*-nitrosoaniline takes place:



The results of spectroscopic analysis showed that the oxygen atom of the nitrosamino-group behaves as the electron donor in these complexes, although the possibility of the involvement of the amino-nitrogen in the formation of the donor-acceptor bond has also been suggested [158].

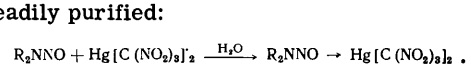
The NMR spectra of the adducts of *N*-nitrosodimethylamine with BF_3, PCl_5, $SbCl_5$, $AlCl_3$, and $ZnBr_2$ showed that the methyl groups are non-equivalent, as in the free nitrosamine. The non-equivalence of the methyl groups is evidence that the amino-nitrogen in the complexes remains in a state of sp^2 hybridisation. Consequently the acceptor is linked to the oxygen atom [197]. This structure is also confirmed by the high dipole moments (7.3 and 7.5 D) of the complexes of *N*-nitrosodiethyl- and *N*-nitrosodipropyl-amines with boron trifluoride.

N-Nitrosodiethylamine forms a 2 : 1 complex with nitrogen tetroxide, which was confirmed by studies of the phase diagram, viscosity, and electrical conductivity of nitrosamine–N_2O_4 mixtures [103,198,199]. On the basis of ultraviolet spectroscopic data, structure (IV) was attributed to the complex [199], but, in the light of the above concepts concerning the structure of nitrosamines, structure (V), where the oxygen atom of the nitrosamino-group functions as the electron donor, is evidently more likely:



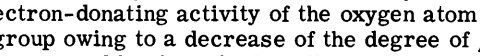
(IV) (V)

Recently it was discovered that *N*-nitrosodialkylamines readily form complexes with di(trinitromethyl)mercury in water [200-202]. The compounds are stable on storage and can be readily purified:

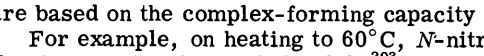


N-Nitrosopolynitroalkylamines, for example *N*-nitroso-di-(2,2,2-trinitroethyl)amine, do not react with di(trinitroethyl)mercury, in contrast to their unsubstituted analogues. This finding can be accounted for by a weakening of the electron-donating activity of the oxygen atom of the nitroso-group owing to a decrease of the degree of p-π conjugation caused by the polynitroalkyl groups.

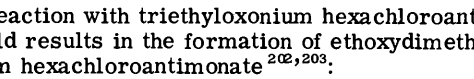
The reactions of nitrosamines with other electrophilic agents are based on the complex-forming capacity of the former. For example, on heating to 60°C, *N*-nitrosodimethylamine reacts with methyl iodide [203]:



The reaction with triethyloxonium hexachloroantimonate in the cold results in the formation of ethoxydimethyldiazonium hexachloroantimonate [202,203]:

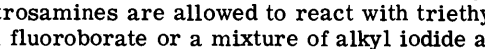


O-Alkylnitrosimmonium salts are formed in high yields when nitrosamines are allowed to react with triethyloxonium fluoroborate or a mixture of alkyl iodide and silver perchlorate [204,205]:



The study of the chemical behaviour of the salts and their infrared spectra showed that they are *O*-derivatives.

Dimethyl sulphate alkylates *N*-nitrosodimethylamine with formation of trimethylnitrosimmonium methyl sulphate. It is interesting that this adduct readily reacts with sodiocyclopentadienyl, forming the monomeric hydrazone of cyclopentadienone [206]:



2. Reduction to *NN*-Substituted Hydrazines

The reduction of the nitroso-group to the amino-group is one of the characteristic reactions in the nitrosamine series. It was discovered by Fischer in the synthesis of dimethylhydrazine [19]. The reaction takes place when an acetic acid solution of *N*-nitrosodimethylamine is treated

with zinc dust. Apart from dimethylhydrazine, ammonia and dimethylamine were isolated. Later diethylhydrazine [207], piperidylhydrazine [208], isobutylmethylhydrazine [209], etc. were synthesised in this way; dimethylhydrazine was obtained in a higher yield [52].

When *N*-nitrosodiethylamine is reduced with the zinc and acetic acid, the formation of tetraethyltetrazene together with diethylhydrazine was observed [210]. A similar reaction was noted in the reduction of nitrosamines with hydrogen in the presence of palladium deposited on calcium carbonate [211]:

$$2\,(C_2H_5)_2N{-}NO + H_2 \rightarrow (C_2H_5)_2N{-}N{=}N{-}N(C_2H_5)_2\,.$$

Several ring-substituted dibenzyl derivatives of hydrazine were described by Curtius [17,212,213] and other investigators [87,88]. Using a modified method of reduction in ethanol and milder reaction conditions, they increased the yields of the desired products to 75%. A number of arylalkyl and dialkyl derivatives of hydrazines were synthesised by the same method [137,214,215].

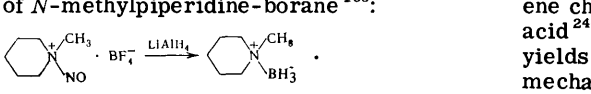
Apart from zinc and acetic acid, sodium amalgam [78,113] and also tin and hydrochloric acid [113] were employed to reduce nitrosamines. In the latter case hydrazine is not formed but the nitrosamine decomposes with elimination of the nitroso-group. The available data on the reduction with sodium amalgam are contradictory. Hydrazinoacetic acid and its dimethyl ester are formed from the corresponding nitrosamines in low yields, while *N*-nitrosodibenzylamine is converted into ammonia and dibenzylamine [113].

The method of reduction of *N*-nitrosodialkylamines with zinc in acetic acid is effective only for methyl-, ethyl-, and propyl-substituted nitrosamines [215]. Starting with the n-butyl derivative, secondary amines appear as the main reaction product. A general method of reduction with lithium aluminium hydride, developed for the synthesis of di-n-propyl-, di-n-butyl-, and di-n-pentylhydrazines as an example [215], has been proposed for the higher *N*-nitrosodialkylamines. Subsequently it was established that the result of the reaction depends on the nitrosamine: lithium aluminium hydride molar ratio. Thus for the reduction of *N*-nitrosodimethylamines the molar ratio of the components must be 1 : 2, [216] and in the case of *N*-nitrosodiphenylamine the ratio must be 1 : 1. [217] The yield of the desired product is affected also by the order of mixing of the components.

It is interesting that in the first stage of the reaction of the nitrosamine with lithium aluminium hydrides coloured complexes are formed, which are converted into dialkylhydrazines only on treatment with water [217,218]:

$$2\,R_2N{-}NO + 2\,LiAlH_4 \rightarrow (R_2N{-}N)_2AlLi + LiAlO_2 + 2\,H_2\,,$$
$$(R_2N{-}N)_2AlLi + 2\,H_2O \rightarrow 2\,R_2N{-}NH_2 + Li\,AlO_2\,.$$

The appearance of side products in the case of aromatic nitrosamines can be explained by the decrease of the polarity of the N–O bond owing to conjugation with the benzene ring. The reduction of *N*-methylpiperidine-nitrosyl fluoroborate with lithium aluminium hydride leads to the formation of *N*-methylpiperidine-borane [106]:



The catalytic hydrogenation of nitrosamines on the palladium catalyst in the presence of iron salts under pressure [219], reduction with zinc and aluminium in the presence of mercury salts or reduction with zinc in hydrochloric acid [220], and other reduction processes [221] have been described. The reaction of *N*-nitrosodialkylamines with zinc dust in formic acid in the presence of mercury(II) chloride results in the formation of an interesting class of compounds–*N*-isocyanodialkylamines [222].

Numerous modifications of the methods of hydrogenation of *N*-nitrosodialkylamines are quoted in the patent literature [223–233]. Compared with catalytic hydrogenation, the reduction of nitrosamines with sodium in liquid ammonia or alcohol [234] gives lower yields of dialkylhydrazines.

Nitrosamines can be reduced electrochemically to the corresponding hydrazines [235–237] or amines with elimination of one nitrogen atom in the form of ammonia. *NN*-Substituted hydrazines are formed via the mechanism

$$R_2NNO + 4\,H^+ + 4e \rightarrow R_2NNH_2\,.$$

The studies on the electrochemistry of nitrosamines have recently been reviewed in a monograph [238] and therefore they will not be discussed here.

When *N*-nitrosodialkylamines are hydrogenated in sulphuric, hydrochloric, nitric, acetic, or oxalic acids in the presence of Group VIII elements on charcoal or silica gel under pressure, hydroxylammonium salts are formed [239].

Nitrosamines undergo far-reaching cleavage on treatment with sodium hydrosulphite in an alkaline medium or when acted upon by lithium in liquid ammonia. This is known as the Overberger–Lombardino reaction and takes place via the intermediate formation of *N*-nitrenes, which readily decompose with evolution of nitrogen:

$$(RCH_2)_2N{-}NO \xrightarrow{Na_2S_2O_4;\,OH^-} (RCH_2)_2N{-}NHOH \xrightarrow[-H_2O]{} (RCH_2)_2N{-}\ddot{N} \xrightarrow[-N_2]{} \rightarrow (CH_2R)_2\,.$$

The Overberger–Lombardino reaction has been discussed in detail in monographs [240,241].

3. Oxidation and Nitration

Nitrosamines are important starting materials for the synthesis of secondary *N*-nitramines. According to the existing hypotheses, this reaction is based on the oxidation of the nitroso-group to the nitro-group.

The use of hydrogen peroxide with nitric acid for the oxidation gives low yields of nitramines and the desired product is contaminated [242]. Best results were obtained when nitric acid mixed with ammonium persulphate was employed [27]. Trifluoroperacetic acid proved to be a very convenient oxidising agent for nitrosamines [243]. The simplicity of the process and the purity and high yields of the final products made the oxidation of nitrosamines with trifluoroperacetic acid a valuable preparative method for the synthesis of secondary nitramines. For example, when *N*-nitrosodiethyl- and *N*-nitrosodibutylamines were acted upon by a mixture of trifluoroacetic acid in 90% hydrogen peroxide, the corresponding *N*-nitramines were obtained in 80% yield. When 30% hydrogen peroxide was employed, the yield of nitramines fell. A mixture of hydrogen peroxide and trifluoroacetic anhydride in methylene chloride may serve as a source of trifluoroperacetic acid [244]. This modification of the oxidation reaction yields pure nitramines in yields of 90% and above. The mechanism of the conversion of nitrosamines into nitramines under the influence of trifluoroperacetic acid has not been investigated:

$$R_2NNO \xrightarrow{CF_3COO{\cdot}OH} R_2NNO_2\,.$$

When *N*-nitrosodiethylamine was oxidised with nitronium pyrosulphate, acetaldehyde and acetic acid were

formed. The oxidation of *N*-nitrosodiethylamine with nitrogen pentoxide is very vigorous. The reaction may be controlled only by diluting the reactants [199]:

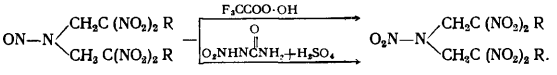
$$2\,(C_2H_5)_2NNO + N_2O_5 \rightarrow 2\,C_2H_5NO_2 + 2\,CH_3COOH + HNO_2 + HNO_3,$$
$$C_2H_5NO_2 + HNO_2 \rightarrow CH_3C(NOH)NO_2 + H_2O.$$

Until recently the reaction of nitrosamines with nitric acid was investigated only for aromatic compounds [245,246]. It has been shown [247] that ethyl *N*-isobutylcarbamate reacts with fuming nitric acid at −80°C to give a mixture consisting of 90% of ethyl *N*-isobutyl-*N*-nitrosocarbamate and 10% of ethyl *N*-isobutyl-*N*-nitrocarbamate. When the *N*-nitroso-derivative is subsequently treated with 100% nitric acid, the *N*-nitrated product is formed. The reaction was not investigated in detail. In other studies [29,144] it was shown that certain *N*-nitrosopolynitroalkylamines are readily converted into the corresponding nitramines under the influence of nitric acid or a mixture of nitric and sulphuric acids:

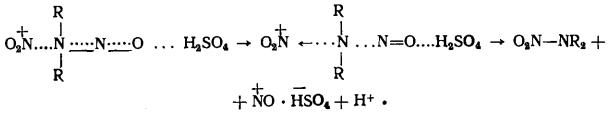
$$[BrC(NO_2)_2CH_2]_2N{-}NO \xrightarrow{HNO_3} [BrC(NO_2)_2CH_2]_2N{-}NO_2.$$

It is important to note that *N*-nitrosopolynitroalkylamines are resistant to oxidation by trifluoroperacetic acid [89,248]. If the oxidation of nitrosamines with trifluoroperacetic acid is assumed to be analogous to the hydroxylation of olefins, the negative results obtained in the oxidation of *N*-nitrosopolynitroalkylamines can probably be accounted for by the deficiency of electrons in the >N⁺⁻N⁺⁻O system owing to the electron-accepting influence of the substituents.

On the other hand, in *N*-nitrosopolynitroalkylamines the N–N bond should be weakened compared with the unsubstituted analogues. This leads to the possibility of an electrophilic substitution of the nitroso-group by a nitro-group in compounds of this kind. We believe that a convincing proof of the substitution of the nitroso-group is provided by the reaction of *N*-nitrosopolynitroalkylamines with nitrourea in sulphuric acid, leading to the formation of *N*-nitro-derivatives [248]. Nitrourea in sulphuric acid is known to be a source of nitronium cations [249]:



The reaction of *N*-nitrosopolynitroalkylamines with nitronium perchlorate in sulphuric acid is also accompanied by the formation of *N*-nitrosopolynitroalkylamines [248]. In an organic solvent (carbon tetrachloride) nitration does not occur. Since the presence of an acid and a nitronium cation is essential for the nitration of nitrosamines, the reaction can probably be described in terms of a "push–pull" mechanism:

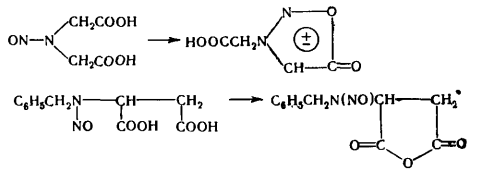


Thus the conversion of nitrosamines into nitramines can be achieved not only by the oxidation of the nitroso-group, but also by its electrophilic substitution by a nitro-group. The latter type of reaction is particularly characteristic of nitroso-derivatives containing electron-accepting substituents, for example polynitroalkyl derivatives.

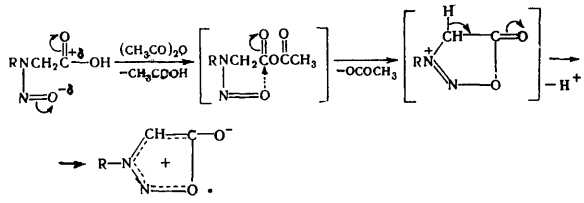
4. Cyclisation of α-Nitrosaminocarboxylic Acids and Their Nitriles into Sydnones and Sydnoneimines

In 1935 Earl and Mackney [250] obtained by treating *N*-nitroso-*N*-phenylglycine with acetic anhydride a cyclic compound, which was called sydnone (in honour of the place where it was first synthesised). Later it proved possible to introduce into the cyclisation reaction the nitriles of α-nitrosaminocarboxylic acids [95], which resulted in the formation of sydnoneimines. The initial discoveries were followed by an intense investigation of the methods of synthesis and properties of this interesting class of compounds. Two reviews dealing with the chemistry of sydnones and sydnoneimines were published [2,3] the second of which appeared comparatively recently and therefore we shall only mention the methods for the mechanism of the cyclisation of nitrosamines into these compounds.

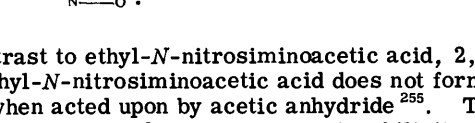
Usually acetic anhydride is employed for the cyclisation. However, trifluoroacetic anhydride, thionyl chloride, and *NN'*-di-isopropylcarbodi-imide can also be used for this purpose [251,252]. *N*-Nitrosodicarboxylic acids, for example nitrosiminodiacetic acid, are cyclised similarly to monocarboxylic acids [253,254], but cases are known where only the carboxy-groups are involved in the reaction [95]:



The formation of sydnones is based on the nucleophilic nature of the oxygen atom of the nitroso-group, and takes place via a mixed anhydride (when anhydrides are employed as the dehydrating agents), which already at room temperature splits off in succession an acetate ion and a proton [2,252]:

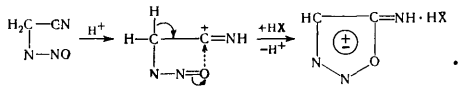


In contrast to ethyl-*N*-nitrosiminoacetic acid, 2,2,2-trinitroethyl-*N*-nitrosiminoacetic acid does not form a sydnone when acted upon by acetic anhydride [255]. This is probably due to the reduction of the nucleophilicity of the oxygen atom in the >N–N=O fragment under the influence of the trinitroethyl group. In the cyclisation of polynitroalkyl-*N*-nitrosaminoacetic acids, it is essential to employ trifluoroacetic anhydride, which increases the electrophilicity of the carbonyl carbon atom in the intermediate mixed anhydride:

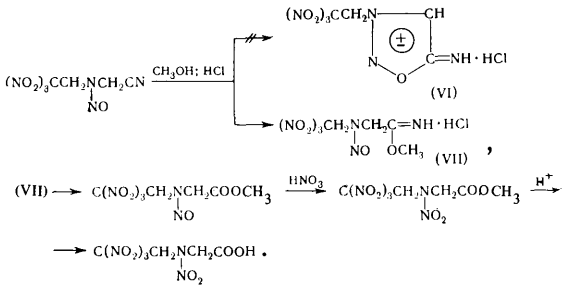


The nature of the cyclisation of the nitrile of α-nitrosaminocarboxylic acids to sydnoneimines is determined by the capacity of the nitrile group to combine with

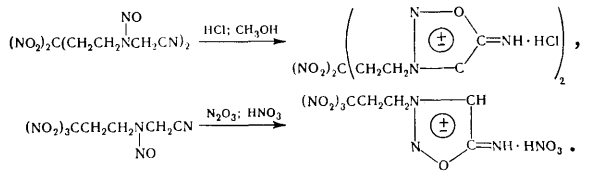
electrophilic agents. The reaction is achieved under the influence of hydrogen chloride [256] or nitrogen oxides [96]:



The powerful influence of the electron-accepting substituents on the conjugation in the >N⋯N⋯O fragment can be demonstrated yet again for the nitriles of polynitroalkyl-*N*-nitrosaminocarboxylic acids as an example. Thus, in attempts to cyclise the nitrile of 2,2,2-trinitroethyl-*N*-nitrosaminoacetic acid in methanol under the influence of hydrogen chloride, the imino-ether (VII) was isolated instead of the expected sydnoneimine (VI), the structure of (VII) being demonstrated unambiguously by its conversion into *N*-nitramino-2,2,2-trinitroethylacetic acid [257]:

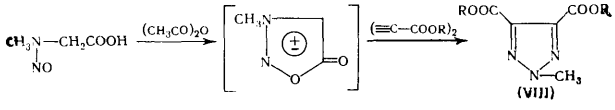


The formation of the imino-ether (VII) is possible only when the nucleophilic properties of the oxygen atom of the nitroso-group are weakened, as a result of which the intermediate carboimmonium ion $(NO_2)_3CCH_2N(NO)CH_2\overset{+}{C}=NH$ undergoes methanolysis, which competes with the ring-closure reaction. The removal of the nitro-groups to the γ-position relative to the nitrosamino-group weakens their influence on the polarisation of the oxygen atom and promotes the formation of the sydnoneimine [257]:

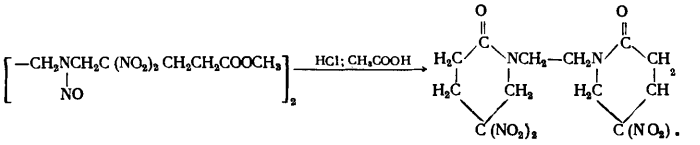


Sydnones and sydnoneimines are reactive mesoionic aromatic compounds. The hydrogen atom in the 4-position in the ring is readily substituted by halogens, nitro-groups, sulpho-groups, etc. Sydnones may be employed to synthesise hydrazines [45]. They undergo the 1,3-dipolar-cycloaddition reaction with unsaturated compounds, forming pyrazoline derivatives [258]. In contrast to sydnones, sydnoneimines undergo ring opening under conditions of alkaline hydrolysis, the amides of α-nitrosaminocarboxylic acids being formed [95]. Sydnoneimines form readily *exo*-*N*-nitroso- and nitro-derivatives.

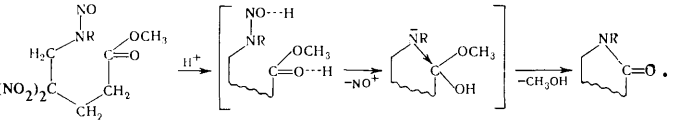
When *N*-nitrososarcosine is heated with acetic anhydride in the presence of acetylenedicarboxylic acid esters, carbon dioxide is evolved and a cycloadduct (VIII) is formed [259]:



Recently it has been established for esters of polynitroalkyl-*N*-nitrosaminocarboxylic acids that yet another type of cyclisation is characteristic of *N*-nitroso-compounds. When *N*-nitrosodi-(4-methoxycarbonyl-2,2-dinitrobutyl)amine and *NN*-dinitrosodi-(4-methoxycarbonyl-2,2-dinitrobutyl)ethylenediamine were treated with a mixture of acetic and hydrochloric acid, *N*-(4-carboxy-2,2-dinitrobutyl)-$\gamma\gamma$-dinitro-δ-valerolactam and ethylenedi($\gamma\gamma$-dinitro-δ-valerolactam) were isolated [260]:

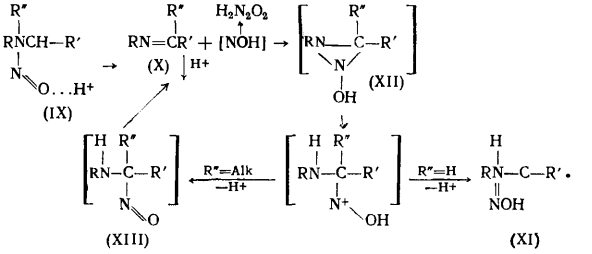


The reaction is accompanied by vigorous evolution of nitrogen oxides. The nature of closure to the lactam ring shows that the nitroso-group is split off as the nitrosonium cation with transfer of the bonding electron pair to the nitrogen atom of the amino-group. The presence of acid promotes the elimination of the nitroso-group and the protonation of the carbonyl carbon atom, while the presence of a five-membered carbon chain at the nitrogen atom creates favourable steric conditions for ring closure. The mechanism of the formation of the lactam ring can be represented as follows:



5. Photochemical Reactions of Nitrosamines

Several years ago reports appeared about a new reaction in the nitrosamine series: photolytic decomposition in the presence of acids [261,262]. On ultraviolet irradiation in methanol or water in the presence of hydrochloric acid, nitrosamines are converted into amidoximes, secondary amines, alkylideneimines, and other compounds. It is suggested that in the first reaction stage a complex (IX) is formed, which decomposes to the imine (X) and a nitroxyl in a solvent cage via an excited triplet radical-ion π-complex. The amidoxime (XI) is formed as a result of the recombination of (X) and NOH. The recombination is possible either via the addition of the monomer of hyponitrous acid and a proton to the C=N double bond of (X) or via the intermediate formation of *N*-hydroxyaziridine (XII) with subsequent rearrangement of the latter to the amidoxime:



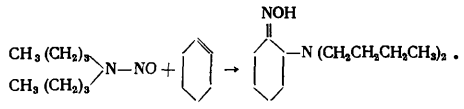
In this case, when the carbon atom of the C=N bond of (X) does not split off a proton (R″ ≠ H), for example in the photolysis of *N*-nitrosodicyclohexylamine, the OH group is lost and a *C*-nitroso-compound (XIII) is formed. Elimination of NOH from (XIII) again leads to the alkylideneimine (X). Therefore the retardation of the nucleophilic attack

on NOH is accompanied by the hydrolysis or polymerisation of the primary photolysis product. It is evident that the steric factor plays an important role in the photoelimination reaction and therefore *trans–anti* elimination of NOH from the photoexcited nitrosamine–proton complex takes place. The intermolecular mechanism of the photoisomerisation of *N*-nitrosodialkylamines has been discussed [263].

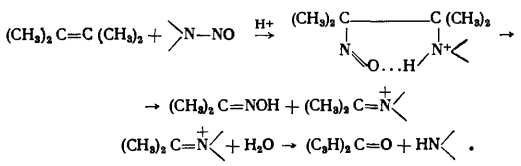
The photolytic decomposition of nitrosamines leads ultimately to the formation of aldehydes and ketones. For example, *N*-nitrosodibutylamine gives a high yield of butyraldehyde after the hydrolysis of the amidoxime (XI), while *N*-nitrosodicyclohexylamine gives rise to cyclohexanone [264].

In the presence of acids the photolytic addition of *N*-nitrosamines to various olefins takes place smoothly [265–267]. Formally the photoaddition reaction takes place via the dissociation of the N–N bond with subsequent addition of the nitroso- and amino-groups to the C=C bond and formation of a *C*-nitroso-compound as the primary reaction product. The latter undergoes secondary reactions, which lead to the final product [265].

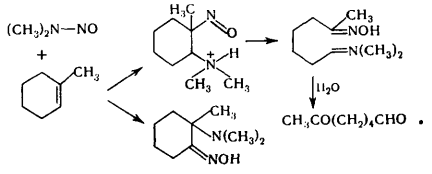
N-Nitrosodibutylamine adds to cyclohexene with formation of the oxime of 2-di-n-butylaminocyclohexanone in 38% yield [267]:



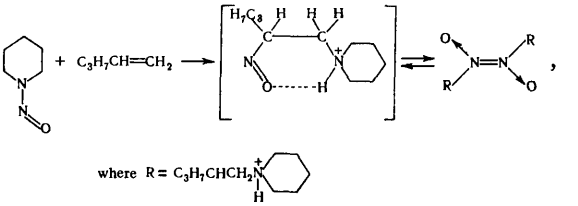
The nitroso-group adds as a rule to the most hydrogenated carbon atom. This observation made it possible to achieve the photolytic addition of nitrosamines to a multiple bond with subsequent dissociation of the C–C bond [266]. Thus irradiation of a mixture of tetramethylethylene and nitrosopiperidine leads to the formation of acetone and acetoxime:



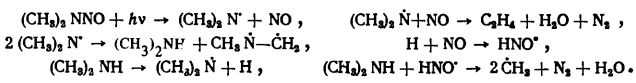
Similarly α-methylstyrene forms acetophenone and di-(1-piperidinyl)methane. When the carbon atom bound to the nitroso-group is combined with a hydrogen atom, the reaction stops at the stage involving the isomerisation of the *C*-nitroso-derivative to the oxime and the C–C bond is not ruptured. Sometimes intramolecular proton transfer can be faster than the isomerisation to the oxime. *N*-Nitrosodimethylamine reacts with 1-methylcyclohexene, forming predominantly 6-oxoheptanal [265]:



The addition of *N*-nitrosopiperidine to pent-1-ene is accompanied by the formation of a dimer of the *C*-nitroso-derivative via the mechanism [265]:



When *N*-nitrosodimethyl- and *N*-nitrosodiethylamines were photolysed in the vapour phase, hydrogen, nitrogen, alkanes, secondary amines, and nitrogen oxides were detected in the reaction products [152]. These results suggest that, in contrast to the low-temperature photolysis, the process has a radical mechanism:



VI. CERTAIN ASPECTS OF PRACTICAL APPLICATION

The lower *N*-nitrosodialkylamines, in particular *N*-nitrosodimethylamine, are largely employed in the synthesis of asymmetric dialkylhydrazines. Dimethylhydrazines are one of the most important components of rocket fuels [268,269]. A mixture of dimethylhydrazine, dimethylamine, and ammonia, obtained by the hydrogenation of *N*-nitrosodimethylamine in the vapour of liquid phase, has been recommended for guided rockets and missiles [228,229].

It has been noted in the patent literature that nitrosamines may be employed as antioxidants in fuels, lubricating oils, and rubbers [98]. There is an interesting prospect of the employment of nitrosamines as special fuels, stabilisers for aromatic halogeno-compounds, fungicides, insecticides, and bactericides and also as intermediates in the manufacture of medicinal preparations [61,98,270].

N-Nitrosodimethylamine is employed in the form of aqueous solutions or powders as a nematocide. In a dose of 112 kg per hectare it protects tomatoes from the nematode *Meloidogyne incognita* and in doses of 56 to 112 kg per hectare it is non-phytotoxic for carrots, tobacco, cabbage, and the cotton plant; however, it inhibits to some extent the growth of [lima] beans and peas [270].

N-Nitrosodimethylamine has been recommended as a solvent in the manufacture of fibre from polyacrylonitrile [271].

However, the high toxicity of nitrosamines should be noted. For example, *N*-nitrosodimethylamine has been included in the group of carcinogenic and irritant substances. It is recommended that the possibility of the contamination of air by this compound be completely prevented [272].

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The Mössbauer Effect and the Study of the Chemical Consequences of Nuclear Transformations

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The present review deals with one of the most important branches of radiochemistry, of considerable practical and applied importance (the preparation of "labelled" compounds, the enrichment of radioactive isotopes) and scientific and theoretical interest. An understanding of processes involving atoms which have undergone a nuclear transformation in the solid phase will make it possible to solve many problems of the physics and chemistry of the solid state. The bibliography contains 151 references.

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I. INTRODUCTION

The history of the study of so-called "hot" atoms, or "recoil atoms" dates from the discovery of Szilard and Chalmers[1]. The extensive practical development of reactor and cyclotron irradiation made the preparation of the radioactive isotopes of many elements and the study of the chemical effects accompanying radioactive decay or the course of a nuclear reaction readily attainable. The forms in which the recoil atoms are stabilised are determined by dissolving the irradiated or labelled solid specimen, followed by radiochemical analysis of the solution containing the radioisotope formed. This method of study is general in character and is obligatory; the concentrations of recoil atoms are so small that the observation of their chemical behaviour is possible in principle only if use is made of their radioactivity. So long as we are interested in practical problems (for example the enrichment of isotopes) no particular objections can be made to the use of an appropriate solvent and carriers. This method, however, acts as a brake on the development of theories of the mechanism and the forms in which recoil atoms are stabilised in the solids themselves. In fact, in general it is impossible, having detected particular chemical forms of the element being studied in solution, to reach the unambiguous conclusion that their behaviour in solution is a consequence of only the radioactive decay or a nuclear reaction in the solid phase. They may obviously also be a consequence of the reaction of the primary decay fragments with the solvent or with one another. The introduction of additional methods of investigation (the study of thermal annealing, the influence of the conditions of dissolution, etc.) can also give complete information on the true state of recoil atoms in a crystal lattice. It is obvious only that the interpretation of results from the chemical effects of nuclear transformations, obtained by these methods, requires an exceptionally careful attitude towards the dissolution procedure. There arises the complex problem of the correspondence between the forms of stabilisation in the solid and in the solution. Unfortunately, most radiochemical studies are carried out without even an attempt to take account of, or even to assume, the possible consequences of dissolution.

It is clear that the introduction of any experimental method which does not require the dissolution of a substance and which gives information on the behaviour of recoil atoms directly in the solid phase is extremely desirable. This additional possibility was provided for radiochemistry by Mössbauer's discovery of the phenomenon of nuclear gamma-resonance (NGR). Since the production of "Mössbauer" levels is always a consequence of some preceding radioactive decay (β-decay, α-decay, K-capture, isomeric transition) or nuclear reaction [(n,γ), (a,p), Coulombic excitation], it may be concluded that emission Mössbauer spectroscopy can be used successfully to study the chemical consequences of nuclear transformations in solids.

Several advantages of the NGR method for the solution of chemical problems can be listed.

1. The forms in which the recoil atoms are stabilised are studied directly in the solid phase.
2. The conditions of Mössbauer experiments are standardised and reproducible (unlike radiochemical techniques, with countless variations in the conditions of irradiation, dissolution, etc.).
3. The observations are made in a range of temperatures (from helium temperatures to $\sim 1000^\circ$K) which is difficult to attain in the irradiation of substances for radiochemical purposes in the usual form, particularly with subsequent chemical treatment of the target.
4. The consequences of a nuclear transformation are studied in a time interval of $10^{-7}-10^{-9}$ s. These intervals are fairly long compared with the duration of the electronic and relaxation processes accompanying the nuclear transformation, but they are still shorter by many orders of magnitude than the time intervals attainable in radiochemistry. Thus the systems studied are "protected" from the annealing phenomena which take place intensively in many instances at the ordinary temperatures and duration of treatment of the targets.

Although almost all information on the NGR method has been obtained by specialist physicists and has not dealt explicitly with radiochemical problems, it is possible to summarise the results obtained and to analyse them from the viewpoint of radiochemistry. Our aim is to discuss the possibilities provided by the use of the Mössbauer effect in the solution of radiochemical problems.

The present review consists of two sections, one of which is devoted to an NGR study of the relaxation times and forms of stabilisation of Mössbauer atoms produced by nuclear transformations characterised by low values of the recoil energy (K-capture, isomeric transitions, and β-decay). The other section is devoted to an examination of the processes of energy loss by recoil atoms during nuclear reactions [(n,γ), (d,p), Coulombic excitation] involving the formation of atoms with high energy. A separate paragraph gives some information on the parameters of NGR spectra required for the subsequent discussion (a more detailed examination of the problems of NGR theory can be found in a number of monographs[2-4]).

II. MÖSSBAUER EFFECT

Let us consider the emission of a gamma-quantum by a nucleus which is in an excited state and is rigidly fixed in a crystal. In this instance the recoil momentum is absorbed not by an individual nucleus, but by the whole crystal, so that the expression for the recoil energy E_R is written in the form

$$E_R = \frac{E_0^2}{2Mc^2},$$

where E_0 is the energy of the gamma-quantum, M the mass of the crystal, and c the velocity of light. It follows from this expression that the recoil energy is negligibly small and that the gamma-quantum carries with it all the energy of the isomeric transition.

The probability density $W(E)$ for the emission of a gamma-quantum with energy E is given by the equation

$$W(E) = \frac{1}{2\pi} \cdot \frac{\Gamma^2}{(E-E_0)^2 + \frac{1}{4}\Gamma^2},$$

where $\hbar/\tau = \Gamma$ is the width of the spectral line, and τ is the lifetime of the excited nucleus. The last equation thus describes the form of the nuclear spectral line.

Let us consider the following experiment. Let us assume that we have a source of monochromatic gamma-quanta (for example a ^{57m}Fe nucleus in stainless steel) which can move at a velocity of $\pm v$ relative to an absorber (^{57}Fe atoms in stainless steel). If the source is stationary, some of the gamma-quanta of the source, passing through the absorber, will be absorbed, and in accordance with the expression for $W(E)$, the absorption will be maximal. If however the source is moving relative to the absorber at a velocity $\pm v$, the energy of the gamma-quantum will be equal to

$$E = E_0 \pm E_0 \cdot \frac{v}{c}$$

and the absorption will decrease. The dependence of the count rate behind the resonance absorber on the velocity of the source relative to the absorber is called the Mössbauer spectrum.

Up to the present we have considered a radiating atom rigidly fixed in a crystal—the recoil energy is negligibly small, and all the gamma-quanta are "Mössbauer" quanta.

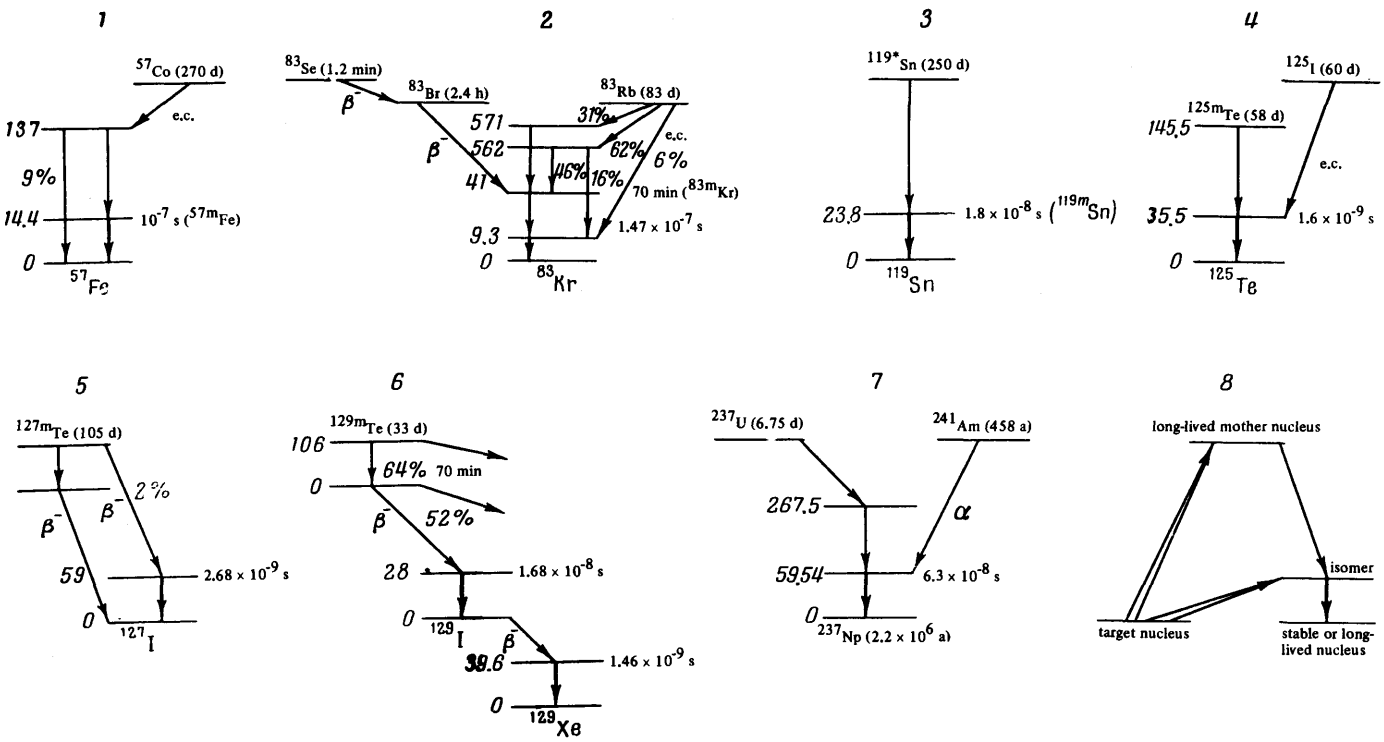

Figure 1. Decay processes leading to the formation of Mössbauer levels: *1*) ^{57}Fe; *2*) ^{83}Kr, *3*) ^{119}Sn, *4*) ^{125}Te, *5*) ^{127}I, *6*) ^{129}I and ^{129}Xe, *7*) ^{237}Np, *8*) general scheme for the formation of a Mössbauer level.

In a real example of gamma-quantum emission, however, the excitation of phonons of the crystal lattice is possible, leading to the partial loss of energy by the gamma-quantum, as a result of which the number of Mössbauer gamma-quanta decreases. The fraction of gamma-quanta emitted by non-phonon transitions is characterised by the quantity f—the Mössbauer coefficient. It is obvious that f characterises the "rigidity" of the lattice, and this coefficient will be small for atoms weakly bound to the matrix (for example, displaced from the normal lattice sites).

The energy of an isomeric transition depends on the electron density at the nucleus, so that for different compounds of the Mössbauer atoms the lines of the NGR spectra relative to a standard absorber (or source) will show a quite definite velocity shift, determined by the valency state (the so-called chemical shift). When the Mössbauer atom is in a distorted environment (different from cubic), the NGR spectrum shows quadrupole splitting, and finally when the M atom is introduced into a magnetic matrix, the phenomenon of Zeeman splitting of the spectrum is possible. Schemes for the formation and decay of various Mössbauer nuclei are given in Fig. 1.

III. THE INFLUENCE OF K-CAPTURE, ISOMERIC TRANSITION, AND β-DECAY ON THE FORMS OF STABILISATION OF A MÖSSBAUER ATOM

As a result of the removal of an electron from the K-shell (or L-, M-, etc. shells) in electron capture or a converted isomeric transition, a singly ionised excited atom is formed; this excitation is removed either by radiative transitions, leading to movement of the vacant position from the K-shell into the L-shell and then to the M-shell, etc., or by the emission of electrons (the Auger effect) leading to the accumulation of a high positive charge in the atom. Since there are a vast number of ways in which cascades of vacancies can develop, the final charge states of the atoms are not the same, that is a spectrum of charges is formed. The actual existence of multiply-charged ions when this process takes place in free atoms has been proved by mass spectrometry[5].

It is assumed that the accumulation of a large positive charge on an individual atom in a molecule produces forces of electrostatic repulsion, as a result of which the molecule dissociates, and the multiply-charged ion is in the "free" state[6]. The subsequent fate of this ion depends on the matrix in which the nuclear process takes place; within a definite time interval it reacts with the surrounding medium and is converted into stable forms (the forms of stabilisation).

There naturally arises the problem of the relaxation times of these highly charged metastable states of the atoms. If these times are much greater than the lifetime of the Mössbauer levels, the NGR emission spectra should contain lines corresponding to these states; if however these times are commensurate with the lifetimes of the Mössbauer levels, the spectra should show broadened lines.

An important feature of radiochemical theory is the assumption that the varied chemical forms obtained in a radiochemical analysis, for example in the study of an isomeric transition, are due to nuclear processes and can be only partly attributed to the influence of the subsequent chemical operations.

The process of β-decay (in the absence of a converted isomeric transition) does not lead to the formation of highly-charged ions, and the chemical changes accompanying β-decay are determined by the essential features of this process (the chemical behaviour of the daughter atom as distinct from the mother atom).

We can consider two basic problems:

1) what are the lifetimes of the metastable highly-charged states?

2) what are the forms in which Mössbauer atoms are stabilised?

1. LIFETIMES OF METASTABLE STATES

In the first moment after the formation of a Mössbauer level as a result of K-capture and an isomeric transition the atom is multiply-charged. It may be assumed that the law for the decay of these states (that is their conversion into the usual valency forms) obeys the exponential relationship[7]

$$I(n) = I_0(n) \exp\left(-\frac{\tau}{\theta(n)}\right),$$

where $I_0(n)$ is the intensity of the n-charged state in the initial moment after the formation of the Mössbauer level, τ the lifetime of the Mössbauer level, and $\theta(n)$ the lifetime of the n-charged state.

It is obvious that the metastable states, the lifetimes $\theta(n)$ of which are comparable with τ, should be revealed in the NGR spectra; the emission lines should be broadened, since[7]

$$\Gamma = \hbar\left[\frac{1}{\tau} + \frac{1}{\theta(n)}\right]$$

Thus the appearance of broadened lines in the emission NGR spectra may indicate that they belong to highly-charged states, the lifetimes of which are comparable with the lifetime of the Mössbauer level.

Electron capture in ^{57}Co has been most extensively studied in this connection. It was noted that if the decay of ^{57}Co takes place in a metal, the NGR spectrum always shows one line, corresponding to an Fe^0 atom (if the matrix is ferro- or antiferromagnetic, the spectrum will of course contain six lines). From this it may be concluded that in metals, in which there is a sufficient number of "free" electrons, the neutralisation of multiply-charged iron ions takes place in a time interval much smaller than 10^{-7} s.[3]

In semiconductors and dielectrics, however, which do not contain sufficient "free" electrons, the neutralisation possibly takes place much more slowly, so that the multiply-charged ions which have not decayed are revealed in the NGR spectrum by the production of a broadened line. This suggestion was put forward by Wertheim[8], when he found that the emission spectrum of cobalt oxide ^{57}CoO (at 295°K) contained two lines, one of which, from the chemical shift, corresponded to bivalent iron, whereas the second (slightly broadened) line corresponded to tervalent iron atoms (Fig. 2). Thus according to Wertheim, the multiply-charged iron ions in cobalt oxide are stabilised as Fe^{2+} (since CoO is isomorphous with FeO), and Fe^{3+} is a metastable form, which is converted into Fe^{2+} in a time interval of $\sim 10^{-7}$ s. More highly-charged states were not detected in the spectrum, and this led Wertheim to the conclusion that their lifetime is much less than 10^{-7} s. The spectra of cobalt oxide were subsequently studied by other workers[7,9-20], some of whom[7] also interpreted their results in terms of metastable states.

A large number of ionic salts of cobalt and iron labelled with ^{57}Co have been studied[13,14,19,21-25]. The studies of the iron salts are of greatest interest, since in this instance it is possible to study both emission and absorption NGR spectra in a single specimen. The two spectra for

$[Fe(NH_4)_2(SO_4)_2.6H_2O]$: ^{57}Co (Fig. 3) show that the absorption spectrum corresponds to only bivalent iron, whereas the emission spectrum shows a characteristic distortion, assigned[23] to the presence of metastable tervalent iron. The emission spectrum of $^{57}CoSO_4.7H_2O$ was interpreted analogously[24]. Finally, the spectrum of $^{57}Co(NH_4)_2(SO_4)_2.6H_2O$, in addition to bivalent and metastable tervalent iron, also showed metastable quadrivalent iron[23].

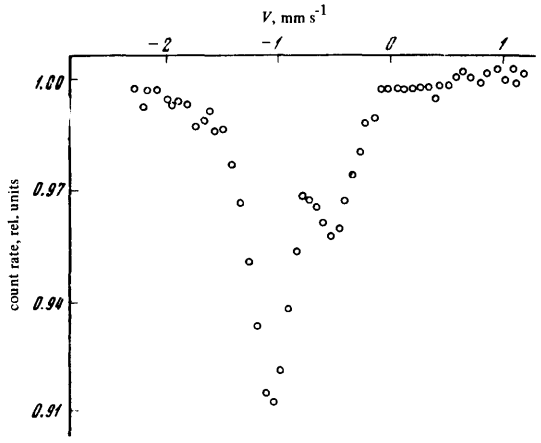

Figure 2. NGR spectrum of ^{57}CoO. Absorber—stainless steel[20].

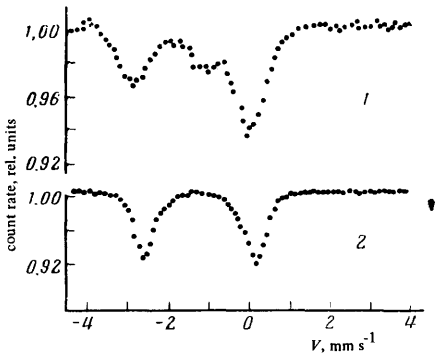

Figure 3. Emission spectrum of $[Fe(NH_4)_2(SO_4)_2.6H_2O]$: ^{57}Co (*1*) and absorption spectrum of $[Fe(NH_4)_2(SO_4)_2.6H_2O]$ (*2*).[14].

While referring the reader to the original papers[7-25] for details, we would point out that the only proof of the production of metastable states after the decay of ^{57}Co is provided by the broadening of the corresponding lines in the NGR spectra. The broadening may, however, be due to some other phenomenon (see below), so that in general, independent experiments which would determine directly the lifetime of these metastable ions are required. Studies of this kind were made by Triftshauser and Craig[12,14,21] for a large number of compounds of cobalt and iron, labelled with ^{57}Co. These involved essentially the application of the method of delayed coincidence; they recorded the gamma-quanta emitted by ^{57m}Fe nuclei in the time intervals (4–43), (43–86), (86–146), and (146–200) ns after the formation of the Mössbauer level (the moment of formation of ^{57m}Fe was recorded by detecting the 122 keV gamma-quantum—see Fig. 1). For the "ordinary" spectrum of ^{57}CoO, recorded without a delay, the authors cited[12,21] obtained $I(+3)/I(+2) \simeq 0.6$ (here $I(+3)$ and $I(+2)$ are the intensities of the Fe^{2+} and Fe^{3+} lines in the spectrum). If it is assumed that tervalent iron is metastable, this ratio should be different for different delay times[26]. It was found[12,21], however, that the ratio $I(+3)/I(+2)$ is independent of the delay time. Analogous results were also obtained for the systems NiO : ^{57}Co, $[Fe(NH_4)_2(SO_4)_2.6H_2O]$: ^{57}Co, $^{57}CoSO_4.7H_2O$, and $^{57}CoCl_2.2H_2O$.[12,14,21]. In other words, the tervalent iron ions formed after the decay of ^{57}Co are also stable, and the time required for the stabilisation of the multiply-charged states of the iron atoms is much less than 10^{-7} s.

Highly charged metastable states similarly were not observed in the formation of other Mössbauer levels (for example for the isomeric transition in ^{119}Sn). It may be concluded with a high degree of reliability that the relaxation times of highly-charged states in solids are much shorter than the lifetimes of the Mössbauer levels (10^{-7}–10^{-9} s).

2. FORMS OF STABILISATION OF MÖSSBAUER ATOMS

a. Electron Capture

It has already been noted that for the decay of ^{57}Co in metals, the NGR spectra in non-magnetic matrices consist of single lines with a chemical shift close to that for Fe^0. This is to be expected, since metals contain sufficient free electrons.

Similarly, in compounds of bivalent iron and cobalt labelled with ^{57}Co we should expect the formation of Fe^{2+}. In fact, in $CoCl_2$, iron is stabilised[13,23,27,28] only in the form of Fe^{2+}, but in $CoCl_2.nH_2O$ (n = 2, 4, or 6) the spectra show characteristic distortion, attributed[23] to the production of tervalent iron ions. Analogous distortions in the NGR spectra of $CoSO_4.7H_2O$, $CoSO_4$, $Co(NH_4)_2(SO_4)_2.6H_2O$, and $[Fe(NH_4)_2(SO_4)_2.6H_2O]$: ^{57}Co were also attributed to the production of tervalent iron[14,23,24], and this may be related to distortion of the structure of the crystal lattice[14] in the environment of the ^{57}Co atom.

An interesting explanation of the distortion of the spectra of $CoCl_2.nH_2O$ was put forward by workers[13] who studied the dependence of the form of these spectra on the quantity of hydrate water in the compound (n = 0, 2, 4, 6) and concluded that the spectrum of $CoCl_2.2H_2O$ consists of the superposition of the spectra of $CoCl_2$ and $CoCl_2.2H_2O$, that is that the distortion of the spectrum is due to the formation of different hydrates of $CoCl_2$.

A large number of studies have been made of the emission spectra of ^{57}Co in various matrices: Co_3O_4, Co_2O_3,[19,20,29,30] NiO,[31-35] MgO,[34-38] MnO,[34,35] CaO,[37,38] CaF_2,[39] $SrTiO_3$,[40] NaF,[22] NaCl,[27,41] AgHal,[42-48] KCl,[49] semiconducting compounds[50-56], and organic compounds of cobalt[57,58]. None of these papers reported the appearance, in the Mössbauer spectra, of lines related to charged states of iron, which would not have been characteristic of the chemistry of iron.

It may be noted that for CoO the production of a tervalent iron line has not yet been fully explained: some

authors [12,14] consider that this is due to the non-stoichiometry of cobalt oxide, whereas others [13,15] suggest that there exist two forms of cobalt oxide—CoO^{I}, in which iron is stabilised in the form of Fe^{2+}, and CoO^{II}, in which Fe^{3+} is stable (for a continuation of the discussion, see Refs. 17, 18, and 59).

K-capture in the case of ^{125}I in copper [60,61] produces in the NGR spectrum only lines corresponding to Te^{0}. For $NaIO_3$, distortion of the spectrum was observed, and this was attributed [60] to the formation of two charged states of tellurium.

Thus the process of K-capture in a solid leads to a limited number of forms of stabilisation of the Mössbauer atom. A characteristic feature of the NGR spectra is their broadening (for example the broadening of the line for tervalent iron in the emission spectrum of cobalt oxide), which apparently indicates a slight difference in the environment of each individual atom.

b. Isomeric Transition

The multiply-charged ions of ^{119m}Sn produced in the conversion of 65.3 keV gamma-quanta in metals and intermetallic compounds are stabilised, as expected, in the form of Sn^{0}. It is obvious that in quadrivalent tin compounds the tin atoms should be stabilised in the form of Sn^{IV}, and this is observed experimentally (for example, tin(IV) oxide, calcium and barium stannates). The situation is more complex for bivalent tin compounds, in which the expected form of stabilisation of the Mössbauer atoms is Sn^{II}. For example, it was found [62] that the emission spectrum of Sn^{II} oxalate shows a bivalent tin doublet, but it was found to be broadened relative to the absorption spectrum of the oxalate, and the magnitude of the effect was smaller; in the opinion of the authors cited, this was due to the existence of some of the ^{119m}Sn atoms in a locally distorted environment. This local distortion may be the result of a strongly converted isomeric transition preceding the Mössbauer transition.

An analogous picture of broadening of the emission spectra of ^{83}Kr has been observed [63-69]. In fact, most mother nuclei of krypton (^{83}Rb, ^{83}Br, and ^{83}Se) decay with the formation of ^{83m}Kr (half-life 70 min). After the converted 31.7 keV gamma-transition, a strongly ionised Mössbauer atom is formed. It is this process which leads to breakdown of the charge symmetry of the ligands and broadening of the ^{83}Kr spectra in dielectrics [66,68]. It was reasonable to assume that processes involving the relaxation of these distortions should take place much more intensively in semiconductors and metals than in dielectrics, and the emission spectra of krypton in this case will have narrow lines. This suggestion has been confirmed [68] (see Table 1).

The isomeric transition in ^{125m}Te in PbTe, metallic tellurium, amorphous tellurium, and tellurium dioxide does not give a set of valency states in the NGR spectra [70,71]. The hydrated compounds H_6TeO_6 and $Na_2H_4TeO_6$, however, show distortions of the spectra†, which were interpreted [71] as due to the production of Te^{IV} atoms together with Te^{VI}. It may be noted that this is not the only possible interpretation, since by analogy with hydrated compounds of cobalt the distortions of the spectra of these compounds may also be due to the formation of a set of Te^{IV} [Te^{VI}? (Ed. of Translation)] with different concentrations of hydrate water.

Thus although the metastable multiply-charged atoms formed after a nuclear transformation are stabilised fairly rapidly (at least in a time interval much shorter than 10^{-7}–10^{-9} s), local distortion of the lattice (as a consequence of the nuclear process) causes each individual atom to have an environment differing slightly from that of the other atoms, and this is responsible for the broadening of the NGR emission spectra and the small magnitude of the effect. It is therefore possible that on dissolution, the atoms which have undergone a nuclear transformation in the solid and have essentially identical chemical character will be distributed in different chemical forms (because of the influence of the nature of the local environment of the recoil atom) in the dissolution process, although the NGR spectrum may correspond to only one state.

Table 1.

Source	Source line width, mm s^{-1}	References
Kr (clathrate)	0.61	66
LiBr	0.65	
KBr	0.75	
NH_4Br	0.87	
$KBrO_3$	1.60	
RbCl	0.70	67
$RbClO_4$	0.85	
ZnSe	0.13	68
PbSe	0.13	

c. β-Decay

The influence of β-decay on the charge states of Mössbauer atoms has been studied for the example of ^{129}I ($^{129}I \xrightarrow{\beta^-} {}^{129m}Xe$). [72-75] It was found that the sources KIO_4 and $Na_3H_2IO_6$ give one line, so that the following compounds are apparently formed:

$$IO_4^- \xrightarrow{\beta^-} XeO_4, \quad IO_6^{5-} \xrightarrow{\beta^-} (XeO_6)^{4-}$$

The β-decay of ^{129}I in $NaIO_3$, $KICl_4.H_2O$, and $KICl_2.H_2O$ gives XeO_3, $XeCl_4$, and $XeCl_2$ respectively; the emission spectra of these products coincide with the absorption spectra. No additional lines were detected (it may be noted that the lifetime of ^{129m}Xe is $\sim 1.5 \times 10^{-9}$ s).

The influence of the β-decay of ^{129}Te on the charge states of ^{129}I has been studied [76-80]. ZnTe, [76-79] tellurium, tellurium dioxide, $Te(NO_3)_4$, [78] and magnesium, calcium, strontium, and barium orthotellurates [80] give spectra corresponding to the existence of one charge state of ^{129}I.

Slightly different results were obtained in a study of the β-decay of ^{127}Te. In ZnTe and tellurium, one charge state of the iodine atoms was detected [76,81-83], whereas in H_6TeO_6 one broad line was obtained; this was attributed [83] to the formation of other products in addition to IO_6^{5-}. It may be noted that for the orthotellurates of the alkaline earth metals (^{129}I NGR) it was found [80] that the width of the spectra depends on the history of the specimens and cannot be attributed to the production of a set of chemical forms of iodine. In this instance [83] the broadening of the spectrum of H_6TeO_6 may be similar in character.

† By distortion of the emission NGR spectrum, we mean a difference between its parameters or form and those of the corresponding absorption spectrum.

Thus emission Mössbauer spectroscopy indicates fairly unambiguously that daughter atoms are stabilised in a time interval much smaller than 10^{-9} s, in an extremely limited set of chemical forms and valencies. The chief role in the production of the large number of chemical forms frequently detected in radiochemical analysis is played by the dissolution process.

IV. PROCESSES OF ENERGY LOSS BY RECOIL ATOMS IN SOLIDS

To describe the chemical behaviour of highly energetic recoil atoms in a solid, models incorporating the results of the radiochemical analysis of irradiated systems and the theories of the mechanisms of energy loss by a "hot atom", developed in solid state physics, are being developed. In was noted in the introduction that the study of "hot" atoms or "recoil" atoms was based on the discovery of Szilard and Chalmers. These historically developed names are explained by the fact that the atoms produced in a nuclear reaction, as a consequence of the law of preservation of momentum, have a recoil energy which is much greater than the energy of the chemical bonding of the atom in the original molecule. Rupture of the chemical bond and decomposition of the mother molecule are thus unavoidable. In the study of the chemical effects of nuclear reactions by radiochemical methods, however, it is often necessary to assume high retention values (up to 100%). Thus it is obvious that the problem of the behaviour of so-called "hot" atoms—the loss of their excess of energy and the interaction with the environment—is a central problem in the study of the chemical consequences of nuclear reactions.

We may note several criteria by means of which radiochemists can judge the value of the theories developed in this field: 1) the ability of the model to give information on the nature of the primary products, that is the changes produced by the recoil atom in its original environment (we have in mind changes in the chemical, electronic, and three-dimensional structures); 2) its ability to reflect the influence of the crystal lattice parameters (that is the individuality of the chemical compound) on the nature of the changes produced; and 3) the ability of the model to establish the relationship between the picture of the changes in the solid and the picture of the distribution of the radioisotope among the different chemical forms in solution.

It should immediately be said that no single theory satisfying these criteria to a sufficient degree has yet been developed in radiochemistry and nuclear chemistry.

The phenomena of "retention" (that is the existence of radioactive atoms in the mother form) and "yield" (that is the existence of radioactive atoms in chemical forms differing from the mother form) are explained in radiochemistry by means of models of various kinds, proposing different mechanisms for the interaction of a hot atom with the environment in a crystal lattice. The principal models of the process of energy loss by recoil atoms have been described in detail[1].

In the "billiard ball" model, the hot atom loses the recoil energy as a consequence of several elastic collisions with the atoms of the lattice. This leads to the idea of a molten region (with an original local temperature of $10^{-6}-10^{-7}$°K) occupying a volume of $\sim 3 \times 10^5$ atoms and existing for about 10^{-8} s. We should expect that partial mixing of the substance in the molten zone would take place and that the distant environment would influence the chemical behaviour of the recoil atom.

The "ligand loss" model assumes the production of a series of charged fragments formed by a hot atom which has left its original environment (for example MnO_3^+, MnO_2^{3+}, MnO^{5+}, and Mn^{7+} in the (n,γ) reaction in potassium permanganate). Although the initial valency of the atom remains the same, the yields of the different chemical forms of the hot atom are attributed to the different reactions of the dissolving medium with the fragments produced in the solid.

The "hot zone" model, based on the theories of solid state physics on the movement of charged particles in a crystal lattice, leads, for example, to the following zone parameters for a recoil atom which has been stopped: for the typical example of an (n,γ) reaction, the volume of the region in the lattice heated above the melting point (~ 1000°K) corresponds to ~ 1000 atoms, and the lifetime of this "hot zone" is $\sim 10^{-11}$ s. It is suggested that the fusion region consists of a superheated solid rather than a melt, although genuine fusion is possible at its centre.

Thus these models indicate the existence of significant collective changes in the region of the arrested hot atom (significant changes in the chemical, electronic, and three-dimensional structures of the environment). According to these models, which are used to explain the variety of chemical forms produced by recoil atoms, the chemical bonding in the original molecule is generally broken, the hot atom is in the "free" state, and in the final analysis its environment is different from that in the mother matrix.

The values of the retention obtained by radiochemical analysis can be explained only by introducing different mechanisms for the conversion of the recoil atoms into the form of the original compound. Four forms of retention are usually considered[6]: preservation of the original bonds in the molecule in the nuclear process—a comparatively rare situation (primary retention), and return to the original chemical form as a result of: reactions of the "hot" atoms by a mechanism of elastic collisions and epithermal reactions of the radioactive atoms (secondary retention), reactions of radiation-chemical synthesis (tertiary retention), and finally thermal reactions of the recoil atoms and processes of thermal isotopic exchange (quaternary retention).

It is obvious that emission Mössbauer spectroscopy (when the Mössbauer transition is a direct consequence of a nuclear reaction in the solid phase) can be used to verify some of the assumptions of these models. Thus the existence of a melt in the zone of the recoil atoms (for the "billiard ball" model) with a lifetime of 10^{-8} s should make it impossible to observe the NGR emission spectrum. If the "ligand loss" or "hot zone" models are realised, extremely significant changes in the spectra are unavoidable, due to the fact that only a very small number of recoil atoms are in a truly initial "mother" environment after $10^{-7}-10^{-9}$ s. In this instance the part of the emission spectrum corresponding to the mother chemical form of the Mössbauer atom in the solid (that is the retention) can be produced only by the recoil atoms which have been preserved in this form by a primary retention mechanism ("the rare case of preservation of the original bonds in the molecule") and by the mechanism of epithermal reactions of the radioactive atoms. Tertiary and quaternary retention cannot contribute to the total retention when the Mössbauer experiment is carried out directly "under the beam" (for example, excitation of the ^{57m}Fe level as a result of (d,p) and (n,γ) reactions and Coulombic excitation). Secondary retention by the mechanism of "hot" atom reactions, as shown above, similarly cannot contribute to the total retention because of the existence of a molten region

in the zone of the recoil atom at the moment of emission of the resonance gamma-quantum.

It is clear that the experimental observation of the Mössbauer effect after a nuclear reaction makes it possible to follow the fate of highly energetic recoil atoms. The actual existence of NGR spectra, and also their parameters, obviously make it possible to discuss the substance of various models of the process of energy loss by hot atoms in a crystal lattice.

1. USE OF THE MÖSSBAUER METHOD TO STUDY PROCESSES OF ENERGY LOSS BY HOT ATOMS

a. Metallic Targets

Coulombic excitation of the ^{57m}Fe level by α-particles with energy 3 MeV in a target of magnetic iron [84-87] did not show a decrease in the Mössbauer coefficient f for the target relative to f for ^{57}Co, introduced by diffusion into stainless steel (the difference was not greater than 5%). Similarly, differences were not observed in the chemical shift and fine magnetic structure of the Mössbauer spectra of the two sources.

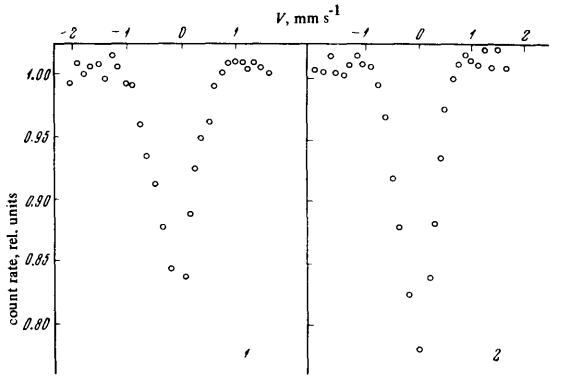

Figure 4. NGR spectrum from a source obtained by the (d,p) reaction in non-magnetic iron (*1*) and from a source obtained by the introduction of ^{57}Co into non-magnetic iron by diffusion (*2*). The background was not taken into account. Absorber—stainless steel [94].

A unique method of Coulombic excitation of the ^{57m}Fe level was used by Sprouse and coworkers [88]: the ^{57m}Fe atoms ejected from a stainless steel target by oxygen ions with energy 36 MeV were passed through a vacuum on to a support of copper, aluminium, gold, or magnetic iron, which thus acted as Mössbauer sources. Comparison of the spectra obtained in this way with the spectra of ^{57}Co introduced into the same matrices showed that the two types of spectra are identical.

It may be concluded that in metals, the atoms which have undergone Coulombic excitation are in the lattice sites for a time interval much smaller than 10^{-7} s, and that their environment does not differ from the environment in the ordinary lattices (otherwise, the magnitude of the effect would decrease, a chemical shift would be observed, and the internal magnetic field acting on the iron nucleus would change). This conclusion is confirmed by analogous results obtained for the Coulombic excitation of the Mössbauer level of ^{61}Ni [89] and the Mössbauer levels of the rare earth elements in metallic targets [90-92]. Thus a metallic ^{184}Yb target has been used as source [91], the metal also acting as absorber. The Mössbauer spectrum consisted of a singlet line, the width of which was greater than that of the natural line by a factor of only 1.3. The magnitude of the effect was $f_{expt} \simeq 0.05 \pm 0.03$, whereas $f_{theor} = 0.08$. All this led to the suggestion [91] that radiation changes do not take place close to the Mössbauer atom. It should be remembered that the recoil energy for Coulombic excitation may reach 100 keV.

The reaction ^{56}Fe$(d,p)^{57m}$Fe in metallic iron has been studied [93-95] (recoil energy ~ 500 keV). The NGR spectra for ^{57m}Fe, obtained by the (d,p) reaction in non-magnetic iron, and for ^{57}Co introduced by diffusion into the same matrix [94] are given in Fig. 4. The results of the treatment of these spectra are given in Table 2.

Table 2.

Parameters of the spectra	Source	
	^{56}Fe$(d,p)^{57m}$Fe	^{57}Co
Chemical shift, mm s^{-1}	0.00	0.00
Amplitude of effect, %	31±4	29±2
Width, mm s^{-1}	0.37±0.04	0.36±0.04

For the ^{57m}Fe source obtained by the (d,p) reaction, a chemical shift relative to the ^{57}Co source in the same matrix is not observed (Table 2). The magnitude of the effect and the width of the line in the spectrum remain unchanged.

For a magnetic iron target, the (d,p) reaction similarly does not lead to a decrease in the effect or to a change in the fine magnetic structure of the NGR spectrum [93-95].

The temperature of the local environment of the ^{57m}Fe recoil atom formed in the (d,p) reaction in magnetic iron was determined [95] from the temperature dependence of the magnitude of the magnetic splitting of the spectrum. In the range of target temperatures between −195° and +40°, the temperature of the environment of the recoil atom was found to be equal to the macro-temperature of the target.

Thus in the (d,p) reaction in a metal lattice, as in the Coulombic excitation examined above, the recoil atoms are produced in a time interval much less than 10^{-7} s, in normal lattice sites, and the temperature of their environment is equal to the macro-temperature. It is obvious that the formation of a molten zone and turbulent mixing of the substance in the recoil zone would have led unavoidably to significant changes in the NGR spectra, but this was not observed experimentally.

The reaction ^{56}Fe$(n,\gamma)^{57m}$Fe in metallic magnetic iron was also studied by the NGR method [96]. The spectrum obtained was the same as the spectrum of ^{57}Co in an analogous matrix, indicating that the ^{57m}Fe atoms after the (n,γ) reaction under the beam (recoil energy $\leq$ 540 eV) are in normal lattice sites. The (n,γ) reaction, carried out under a neutron beam for ^{155}Gd and ^{157}Gd [97] and for ^{39}K [98,99] in metallic targets similarly does not lead to the production of displaced Mössbauer atoms.

b. Non-metallic Targets

Experiments on the study of various nuclear reactions by the NGR method in non-metallic targets are of the greatest interest for the solution of chemical problems of the behaviour of hot atoms in solids.

The Coulombic excitation of the ^{57m}Fe level in Fe_2O_3 showed a decrease in the quantity f for this source relative to f for the source Fe_2O_3 : ^{57}Co. [85-87] The fine structure of the spectrum of the Fe_2O_3 target remains unchanged, as does the chemical shift. The authors cited [85-87] suggest that some of the ^{57m}Fe recoil atoms, after Coulombic excitation, are displaced from the normal lattice sites, leading to a decrease in f. There are no grounds for assuming the possibility of the production of molten zones on energy loss by the hot atom; if this were the case, the NGR spectrum would show a change in fine structure and a chemical shift.

Analogous results were obtained for the Coulombic excitation of the Mössbauer level in ^{73}Ge. [100-102] The decrease in f for the target cannot be attributed to the existence of a hot zone, since the width of the spectrum would have increased [101].

Coulombic excitation of the ^{174}Yb Mössbauer level in Yb_2O_3 [91] gave a spectrum identical to the absorption spectrum of Yb_2O_3. The authors cited [91] concluded that the greater part of the ^{174}Yb atoms after the Coulombic excitation remain in the lattice sites.

The $^{56}Fe(d,p)^{57m}Fe$ reaction in non-metallic targets leads to a decrease in f relative to f for ^{57}Co in the same matrices [95].

The $^{56}Fe(n,\gamma)^{57m}Fe$ reaction in Fe_2O_3 and $FeSO_4.7H_2O$ led to a slight change in the NGR spectra of these targets relative to the spectrum of ^{57}Co in Fe_2O_3 and the absorption spectrum of $FeSO_4.7H_2O$. For Fe_2O_3, a slight decrease in the effective magnetic field acting on the iron nucleus was observed, and for $FeSO_4.7H_2O$ a line characteristic of tervalent iron appeared [96]. This indicated the production of displaced atoms in the targets; for $FeSO_4.7H_2O$, these atoms may also be stabilised in the form of Fe^{3+}.

It should be emphasised that even in such complex compounds as Fe_2O_3 and $FeSO_4.7H_2O$, a considerable proportion of the recoil atoms remain in the normal lattice sites, that is their environment after the (n,γ) reaction is the same as the original environment.

In a study of the (n,γ) reaction under a neutron beam for ^{157}Gd and ^{155}Gd isotopes by the NGR method, it was established that in oxide targets (unlike metallic targets) a slight change in the spectrum is observed; a possible reason for this is that some of the recoil atoms are in displaced positions [97].

It has been shown [98] that, for example, for a source in the form of a KCl target [the reaction $^{39}K(n,\gamma)^{40}K$] the magnitude of the effect is close to the theoretical (f_{expt} = 0.11 ± 0.02, f_{theor} = 0.12 at 80°K), and the width of the spectrum differs little from the theoretical. This may confirm that in the reaction $^{39}K(n,\gamma)^{40}K$ in KCl, the greater part of the potassium atoms at the moment of emission of the Mössbauer gamma-quantum ($\tau \simeq 4 \times 10^{-9}$ s) are in lattice sites. It may be noted that the recoil energy in this case reaches 800 eV.

Various complex compounds of potassium, for example $KAlSi_3O_8$, have been used as targets for irradiation by neutrons [99], but all the spectra consisted of a single line, the width of which exceeded the natural width by a factor of not more than 1.3. This indicates again that there are no significant radiation changes in the environment of an atom which has undergone an (n,γ) reaction.

The $^{118}Sn(n,\gamma)^{119m}Sn$ reaction in tin oxide under conditions of prolonged reactor irradiation has been studied [62,103]. It was found that the spectrum of irradiated ^{118}SnO, in addition to the Sn^{II} doublet, contained a weak Sn^{IV} line. The spectrum of the same specimen, dissolved in hydrochloric acid and frozen, showed a marked increase in the intensity of the Sn^{IV} line (Fig. 5). This is apparently related to the fact that in the (n,γ) reaction under the conditions of prolonged irradiation in a reactor, some of the recoil atoms are displaced, and the intensity of the line from these tin atoms is slight when the spectrum is dissolved. All the radiating atoms are in identical conditions, and this leads to an increase in the intensity of the Sn^{IV} line.

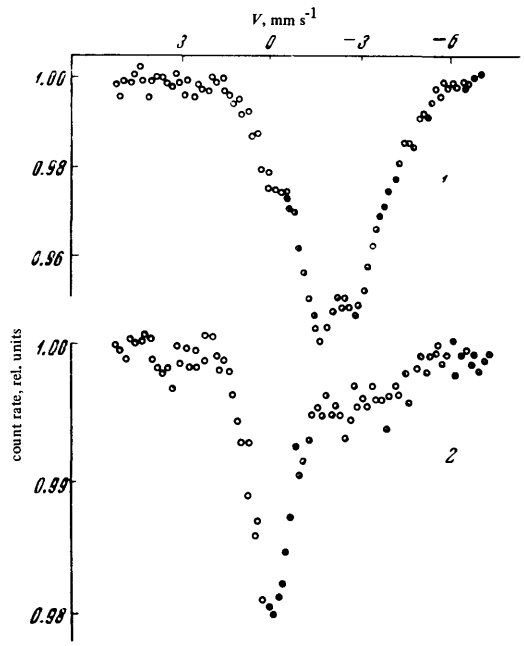

Figure 5. NGR spectra of ^{118}SnO, irradiated in a reactor, at 80° K (*1*) and a hydrochloric acid solution of the same specimen at 80°K (*2*). Absorber—calcium stannate [62].

Slightly different results were obtained for the reactor irradiation of ^{118}SnO and $^{118}SnO_2$, [104] when complex NGR spectra were obtained. The results were interpreted in terms of the "hot" zone model. Later work [62], however, did not confirm these results.

Interesting results were obtained in a study of α-decay in ^{241}Am. [105-111] The spectrum of $^{241}AmO_2$ in NpO_2, and for comparison the spectrum of $^{237}UO_2$ in NpO_2 (the β-decay of ^{237}U gives the same Mössbauer level ^{237}Np), [105] are given in Fig. 6. It can be seen that the effect is much smaller for α-decay than for β-decay. Since the recoil energy after the α-decay of ^{241}Am is ~ 93 keV, displacement of some of the daughter atoms from normal crystal lattice sites is possible, and this decreases the value of f. The theory of the Mössbauer effect after α-decay has been developed [112] and it has been shown that relaxation processes may be responsible for the broadening of the line.

Thus the existence of emission Mössbauer spectra after nuclear reactions characterised by high recoil energies [Coulombic excitation, α-decay, (d,p), and (n,γ)] clearly indicates that a considerable proportion of the recoil atoms, at the moment of emission of the resonance gamma-quanta, are in normal lattice sites. The existence of molten regions, mixing of the substance, and the production of significant radiation damage in the region of the recoil atom are not confirmed. It of course follows from these spectra that some of the recoil atoms after the nuclear reaction are in a local environment which is different from the mother environment, and this is revealed by broadening of the lines and a decrease in the effect.

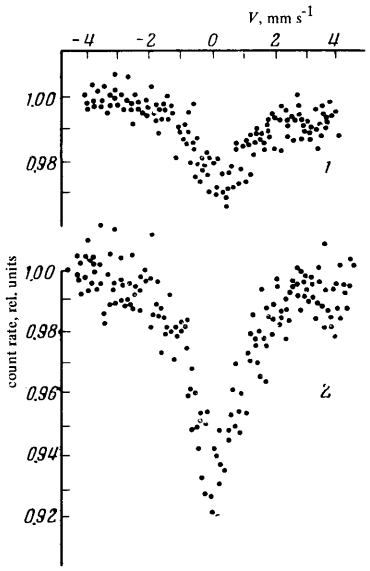

Figure 6. NGR spectra of $^{241}AmO_2$ (*1*) and $^{237}UO_2$ (*2*). Absorber—NpO_2.[105]

The next paragraph describes briefly studies carried out in the last ten years in the field of the physics and chemistry of the solid state, the essential feature of which is the departure from models based on a description of significant changes in the region of the arrested hot atom.

2. PRESENT IDEAS ON PROCESSES OF ENERGY LOSS BY RECOIL ATOMS

We shall try to follow the analogy in the results of the following studies: 1) the solution of the problem from the equilibrium and dynamics of the formation of defects in the crystal lattice; 2) the determination of the parameters of the reaction zone of the recoil atom by radiochemical experiments; and 3) the study of chemical effects in crystals bombarded with accelerated ions.

About ten years ago, theories of so-called crowdions and focusons—new mechanisms of the transfer of atoms and the energy of atoms in crystals—were put forward [113-117]. These theories have been confirmed by calculations on electronic computers [118,119] and by comparison of the results with experiment.

Among the many conclusions following from these calculations, the following is of particular interest: the propagation of the energy of the primary atom in the crystal does not produce phenomena resembling fusion or the turbulent mixing of atoms. Calculations for the recoil energy characteristic of the (n,γ) reaction do not confirm the existence of high temperatures, continuation of the existence of a hot zone, or the collective nature of the changes.

To verify these ideas regarding the dynamics of radiation damage, radiochemical experiments were carried out to determine the parameters of the reaction zone of the recoil atom [the (n,γ) reaction].[120-124] The homogeneous mixed crystals $K_2ReBr_6-K_2SnCl_6$; $K_2ReCl_6-K_2SnBr_6$; $K_2OsBr_6-K_2SnCl_6$; and $K_2ReBr_6-K_2OsCl_6$ were studied. The systems were irradiated with neutrons, and the products of the $^{185}Re(n,\gamma)^{186}Re$ reaction were determined quantitatively (by ionophoresis). For the $K_2ReBr_6-K_2SnCl_6$ system, for example, the K_2ReBr_6 concentration was varied in the range 1–28 mole %. The essential features of the experiments were as follows. The primary retention should be represented by the form of $ReBr_6^{2-}$ retained by the billiard ball mechanism at low concentration of K_2ReBr_6—in the form of $ReCl_6^{2-}$, and for retention by the hot zone mechanism we should expect a set of all forms of hexabromochlororuthenates $ReBr_{6-n}Cl_n^{2-}$ $(6 \geqslant n \geqslant 0)$ with the conditions that the K_2ReBr_6 concentration is not too small.

Analysis of the results led to the following conclusions: 1) the billiard ball mechanism does not apply in any of the systems studied; 2) the concept of fusion in the reaction zone of the recoil atom is refuted, since otherwise the distribution of the yields of all possible bromochlororuthenates should have been close to the random distribution, and this is not observed; and 3) the region of the reaction zone of the recoil atom is smaller and broken down to a smaller extent than is assumed in the hot zone model; fusion processes and significant turbulent mixing of the atoms do not take place in the reaction zone.

Let us now consider experiments on the study of chemical reactions with accelerated ions[125]. These experiments make it possible to compare the results for the chemical distribution of ^{51}Cr atoms in different compounds of chromium subjected to bombardment by accelerated $^{51}Cr^+$ ions or irradiated with thermal neutrons. The results[125] show that the same radioactive products are obtained on dissolution of the crystals after both experiments, and also that a similarity is observed in the kinetics of formation of the $^{51}CrO_4^{2-}$ fragments on thermal annealing (that is complete similarity in the processes of increase in retention on annealing in the two experiments). In the opinion of the authors cited[125], this similarity confirms the hypothesis that the changes in the valency state of radioactive atoms on annealing reflect processes of electronic rearrangement in the crystal in the zone of the ^{51}Cr atom rather than restoration of the altered original molecule. It may be assumed that this conclusion confirms indirectly the theory that the changes produced by a recoil atom in a crystal lattice are small and purely local.

V. THE "SOLID–SOLUTION" PROBLEM

As already noted, one of the fundamental problems in the comparison of information obtained in the study of a solid and its solution is the determination of the influence of the solvent medium on the crystal. It is hoped that the use of the NGR method will provide new and promising possibilities in this connection. The use of other indirect methods to determine the nature of the environment of a recoil atom, not related to the dissolution procedure, is also of interest.

Promising possibilities are provided by the study of the angular correlation of cascade radiation as applied to the chemistry of hot atoms. Thus for $KReO_4$ crystals irradiated with neutrons, considerable breakdown of the angular correlation of the gamma-quanta of ^{188}Re was observed[126]. In the opinion of the authors cited, this indicates that irradiated $KReO_4$ contains forms of ^{188}Re different from the mother form. Nevertheless, chemical analysis of irradiated perrhenates shows 100% retention. This example appears sufficiently clear and demonstrates in this specific instance the "incompatibility" of information obtained before and after dissolution. An interesting feature is that the observed breakdown of the angular correlation to some extent agrees with the information obtained from emission Mössbauer spectroscopy, where the broadening of the lines and the decrease in the magnitude of the effect are attributed to the existence of some of the radiating Mössbauer atoms in an environment different from the mother environment.

In the comparison of the results obtained by the NGR method (and "physical" methods in general) and radiochemical results, allowance must also be made for possible changes in the initial distribution of the chemical forms of the hot atoms in the crystal, depending on the accumulated radiation dose, the extent of the defect character of the original specimens, the irradiation parameters, processes of thermal and radiation annealing, and a number of other factors.

Thus a study of the irradiation of $H_2TeO_4.0.36H_2O$ and H_2TeO_4 in a reactor established[127] that the yield of reduced forms of ^{131}I (the target was dissolved in aqueous KOH solution containing various iodine carriers) increases with increase in the integral neutron flux and the dose of accompanying gamma-radiation.

A study of the neutron irradiation of crystalline tellurium dioxide showed that the increase in the yield of reduced forms of ^{131}I is related to the effect of gamma-irradiation. It was proved[128] that the increase in the yield of reduced forms is due to the reduction of IO_3^- to I^- by reaction with elementary tellurium, formed by the gamma-irradiation of tellurium dioxide.

In the irradiation of $KSb(OH)_6.H_2O$ with thermal neutrons, the retention in the forms Sb^{3+} and Sb^{5+} depends on the quantity of water in the specimens[129].

From these examples it is clear that the borrowing of information from the radiochemistry of a given element for the interpretation of NGR spectra, and naturally the reverse borrowing, are in general inapplicable. Comparison of the results obtained by the two methods is desirable and allowable when the same specimens are studied, with detailed allowance for possible complicating features.

Examination of the information obtained by emission Mössbauer spectroscopy establishes some general features in the consequences of seven forms of nuclear transformation in solids [electron capture, isomeric transition, α-decay, β-decay, Coulombic excitation, and (n,γ) and (d,p) reactions].

1. The metastable highly-charged states of atoms produced as a consequence of nuclear transformations in a solid are discharged in a time interval much smaller than the lifetime of a Mössbauer level ($10^{-7}-10^{-9}$ s) and are converted into stable forms characteristic of the macrochemistry of the given element.

2. The emission Mössbauer spectra generally correspond to an extremely limited set of forms of stabilisation of the recoil atoms (one or two), whereas the use of delicate analytical procedures in radiochemistry often reveals a rich spectrum of chemical forms and valencies. This "discrepancy" is apparently related to the influence of the local environment of the recoil atom (revealed in the emission NGR spectra by broadening of the lines and a decrease in the magnitude of the effect) on the distribution of the radioisotope being studied among different chemical forms during dissolution.

3. The study of the processes of energy loss by hot atoms by Mössbauer spectroscopy does not show the existence of molten zones and mixing of the substance in the reaction region of a highly energetic recoil atom. Even in comparatively complex compounds at high recoil energies, a considerable proportion of the Mössbauer atoms at the moment of emission of the resonance gamma-quantum are in the normal sites of the crystal lattice, and their environment does not differ from the original environment.

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In the two years since the review was written, a large number of papers on the use of the Mössbauer effect to study the after-effects of nuclear transformations in solids have been published. Of work by Soviet authors, mention must first be made of the studies by Nesmeyanov and coworkers[130-132], who investigated the influence of the converted isomeric transition in ^{125}Te and electron capture in ^{125}I on the chemical state of the daughter atoms. Anomalous charge states of Te were not detected, and stabilisation takes place in the usual forms of the macro-chemistry of this element.

The emission spectra of tin in alkali metal and silver halides have been studied[133,134]; no influence of the strongly converted isomeric transition in the 250-day isomer ^{119}Sn on the charge state of the daughter atoms was detected. Similarly, proof was not obtained for the existence of after-effects of electron capture in impurity ^{57}Co atoms introduced into the CoS lattice[135] and semiconducting compounds $A^{III}B^{V}$.[136] The problem of the influence of nuclear transformations on the chemical state of impurity tin and iron atoms in ionic crystals has been studied[137]. It is suggested that the absence of after-effects is related to the "rigidity" of the lattice of the matrices studied (a measure of this "rigidity" is provided by the Debye temperature). Murin and coworkers[138] assume as a working hypothesis that on obtaining recoil energy much greater than the energy of the bond formed by the atom in the lattice, a daughter atom may not leave the lattice site, because of breakdown of the correlation between the momentum and the energy of recoil.

Outstanding among work by authors in other countries is a paper[139] describing a detailed study of the influence of electron capture and β-decay on the chemical state of daughter atoms. The authors cited[139] consider that the changes in the local environment of atoms which have undergone a nuclear transformation (and hence the production of a large number of chemical forms of the daughter atoms) may be observed in lattices with low Debye temperatures or in lattices with a high concentration of defects (irrespective of the magnitude of the Debye temperature). It is suggested that stabilisation of the hot atoms leads to electronic structures characteristic of the macro-chemistry of the given element.

The problem of determining the lifetimes of the metastable states of ^{57m}Fe atoms formed after the decay of ^{57}Co in Cu_2O, MgO, and Al_2O_3 lattices has been studied[140]; it was shown that the iron atoms are stabilised in the usual valency states in time intervals much smaller than the lifetime of the Mössbauer level.

The Mössbauer effect has been studied for atoms which have undergone a nuclear reaction accompanied by a high recoil energy: the $^{56}Fe(n,\gamma)^{57}Fe$ reaction in metallic iron and Fe–Al alloys[141,142]; the α-decay of ^{241}Am;[14] and the Coulombic excitation of various nuclei[144-151]. Although the number of papers devoted to nuclear transformations accompanied by vast recoil energies is increasing rapidly, the problem of the behaviour of recoil atoms of this kind still remains a subject for discussion.

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Formation of Network Polymers

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Methods of analysing the formation of network polymers from polyfunctional compounds and determining their structural parameters are surveyed, and experimental data obtained by these methods on the formation of network polymers from monomers and oligomers are examined. The data permit assessment of the possibilities and the establishment of general laws for the formation of polymer networks in the initial and the final stages of the reactions. The problems of the controlled synthesis of network polymers from polyfunctional compounds are discussed on the basis of the experimental results which have accumulated. The list of references comprises 114 items.

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I. INTRODUCTION

Advances in the synthesis of linear polymers and investigations of their structure stimulate the development of methods for the detailed study of network polymers. Establishment of the laws governing the formation and the structure of network polymers and also the discovery of methods for their controlled synthesis would promote a rational approach to the control of technical processes in the manufacture and processing of materials based on them, since network polymers, unlike linear polymers, are usually formed in the course of these processes.

According to the definition given long ago by Staudinger [1] network (spatial or three-dimensional) polymers are those in which the component chains are joined by chemical bonds in three directions. Among all the types of chemical and physical bonds only covalent bonds are able to form a spatially fixed structure, which is irreversible after breakdown. Other bonds, including ionic and coordinate bonds, are labile and delocalised in space, and may form three-dimensional structures, such as e.g. in ionomers, polycoordinate polymers, etc. Therefore the term "network polymers" should be applied only to polymers whose chains form a network of covalent bonds distributed in space, the so called polymer network. All other types of interaction—ionic, coordinate, hydrogen, or intermolecular bonds, physical contact and entanglement—may also appear in the polymer network, and make their contribution, often very considerable and even predominant, to its formation, structure, and properties.

Polymers which contain a large number of strong but labile bonds (ionic, coordinate, hydrogen, etc.) between the linear chains formed by covalent bonds, and which under certain conditions possess properties characteristic of network polymers, must be regarded as quasi-network polymers.

Network polymers can be obtained by cross-linking existing linear macromolecules with covalent bonds and also by introducing polyfunctional monomers, oligomers, or mixtures thereof into the reaction. Macromolecules can be combined by covalent bonds only when the polymer chains are flexible. In practice this method is applied only in the vulcanisation of elastomers. The second method is generally applicable, and enables network polymers to be obtained with almost any properties—from elastomers with an open network to the so-called "hardened" polymers with a dense network. Recently, therefore, work has been developed especially intensively in this direction. Broad investigations are being conducted into the laws of the formation of polymer networks by reactions of polyfunctional compounds, methods are being developed for the direct investigation of the structural characteristics not only of open-network but also of dense-network polymers, and ways are being studied for the directed synthesis of network polymers having a specified structure and properties. The present paper attempts to summarise the principal results obtained in these investigations.

II. METHODS FOR ANALYSING THE FORMATION OF NETWORK POLYMERS AND ESTIMATING THEIR STRUCTURAL PARAMETERS

Flory [2,3] applied a statistical method for analysing the formation of network polymers by the polycondensation of monomers containing more than two functional groups in the molecule. He correlated the degree of conversion P of the functional groups with the probability of branching of the polymer chains during their growth (branching α coefficient). The following relations exist between P and α in the reaction systems which are encountered most frequently.

1. For a polyfunctional monomer RA_f, whose functional groups react with one another,

$$P = \alpha \qquad (1)$$

2. For a mixture of a polyfunctional monomer RA_f with a difunctional monomer $R'B_2$, where the groups A react only with the groups B, we have

$$P_A = \sqrt{\frac{\alpha}{r}} \qquad (2) \quad ; \qquad P_B = \sqrt{\alpha \cdot r} \qquad (3)$$

where P_A and P_B are the degrees of conversion of groups A and B respectively, and

$$r = \frac{n_A f_A}{n_B f_B},$$

is the ratio of the initial components, n_A, n_B, and f_A, f_B being respectively the numbers of moles and the functionalities of the monomers A and B.

An infinite three-dimensional network of the monomer units interconnected by covalent bonds is formed (gel point) at a critical value of the branching coefficient

$$\alpha_{crit} = \frac{1}{f-1} \quad (4)$$

where f is the functionality of the polyfunctional compound. Until the gel point is reached, values of α lie in the range $0 < \alpha < \alpha_{crit}$.

In the polycondensation of the above reaction systems gel formation occurs ideally when conversion of the functional groups corresponds in Eqns. (1)–(3) to the critical value of α. Thus in the polycondensation of a trifunctional monomer gel formation starts when the degree of conversion of the functional groups is one-half, the corresponding conversion for a tetrafunctional monomer being one-third.

In the polycondensation of a polyfunctional monomer with a difunctional monomer a polymer network is formed only if $\frac{1}{2} < r < 2$. When $r = 1$,

$$P_{A,g} = P_{B,g} = \sqrt{\alpha_{crit}}. \quad (5)$$

where $P_{A,g}$ and $P_{B,g}$ are the degrees of conversion of groups A and B respectively at the gel point.

Statistical analysis of polycondensation beyond the gel point enables the proportion by weight of the sol W_S (the quantity of reaction products unattached to the polymer network) to be related to the coefficient of branching α, and hence to the degree of conversion of the functional groups—Eqns. (1)–(3) and (5):

$$W_s = \frac{(1-\alpha)^2\alpha'}{(1-\alpha')^2\alpha} \quad (6)$$

where $\alpha' < \alpha$ for any physically meaningful value of β in the equation $\beta = \alpha(1-\alpha)^{f-2}$, in which β is an arbitrary quantity in the range $0 < \beta < \alpha_{crit}(1-\alpha_{crit})^{f-2}$. The value of α beyond the gel point lies in the range $\alpha_{crit} < \alpha < 1$. Thus in the polycondensation of a trifunctional monomer $\alpha_{crit} = \frac{1}{2}$ and $\beta = \alpha(1-\alpha)$. For any β in the range $0 < \beta < \frac{1}{4}$, we have $\alpha' = 1-\alpha$, and then

$$W_s = \frac{(1-\alpha)^3}{\alpha^3} \quad (7)$$

Reactions of polyfunctional monomers involving step-by-step (migration) polymerisation conform to similar statistical laws [4,5].

Statistical analysis of the polymerisation of polyvinyl monomers with isolated double bonds, which is propagated by a chain mechanism, presents considerably greater difficulties [6–10]. This is due to the complexity of allowing statistically for different mechanisms of termination of growing macroradicals or macroions. In the simplest case of the copolymerisation of monovinyl and divinyl derivatives the degree of conversion of double bonds at the gel point can be calculated from the equation [6,7]

$$\beta_{crit.} = \frac{1}{\lambda(P_W - 1)} \quad (8)$$

where β_{crit} is the proportion of double bonds which have reacted at the gel point, P_W is the weight-average degree of polymerisation at the gel point, and

$$\lambda = \frac{2M_2}{M_1 + 2M_2}$$

is the proportion of the double bonds in the reaction system which is due to the divinyl monomer, M_1 and M_2 being the numbers of moles of mono- and di-vinyl monomers respectively. No statistical analysis has been made of the reactions of polyvinyl monomers outside the limits of gel formation.

The structure of the polymer network following the gel point is characterised by the frequency (density) of branch points in it, which is expressed by the concentration of effective chains, i.e. those joining two branch points, or by the average length of the chain segment between them. The concentration of chains is expressed as the number of chains N_C or the number of moles of chains n_C in unit of volume of the polymer. The length of the effective chains is estimated as the conventional mean molecular weight M_C of the segment of polymer chain between adjacent branch points. These parameters are interrelated as follows:

$$n_c = \frac{N_c}{N_A} = \frac{\rho}{M_c} \quad (9)$$

where N_A is Avogadro's number and ρ the density of the polymer.

Calculation of the structural parameters of the polymer network expected theoretically from the composition of the initial reactants and the extent of reaction after gel formation will depend on how the structure of the network is represented. A polymer network can be regarded as a combination of chain segments attached at both ends (effective chains), and segments attached at only one end (ineffective chains), to branch points in the network. In the polycondensation of a trifunctional monomer RA_3 with a difunctional monomer $R'B_2$, provided that the groups A react only with the groups B, the number of moles of effective chains after gel formation can be related statistically to the degree of conversion by the formula [11].

$$n_c = \frac{3}{2}\left[P^3\left(1-\frac{q^6}{P^6}\right) - 3q^2P\left(1-\frac{q^2}{P^2}\right)\right] \text{ moles of A} \quad (10)$$

where P is the degree of conversion of groups A and $q = 1 - P$ the proportion of groups A which have not reacted.

In the reaction of a difunctional compound with a small amount of a polyfunctional compound the polymer network can be regarded as comprising long chains formed by the difunctional monomer units and joined together by units of the polyfunctional monomer, which in this case can be regarded as points of a tetrahedral network. The number of moles of effective chains in unit volume of the polymer to be expected theoretically from the composition of the reaction system when the reaction has gone to completion can then be estimated by means of the equation [12,13]

$$n_c = Z \cdot \varepsilon \cdot C \quad (11)$$

where $Z = \frac{1}{2}f$ is the mean number of chains per molecule of an f-functional monomer, ϵ the fraction of the f-functional monomer which has reacted with all the functional groups, and C the number of moles of the f-functional monomer per unit volume of the reaction mass.

In the particular case of the copolymerisation of a monovinyl monomer with a small quantity (up to 3 mole %) of a divinyl monomer, with complete conversion of the double bonds, the number of effective chains per unit volume of the polymer is [14]

$$N_c = \frac{2\rho[M_2] \cdot N_A}{(1-[M_2])M_1 + [M_2] \cdot M_2} \quad (12)$$

The mean molecular weight of the effective chains is calculated as [15]

$$M_c = \frac{2M_1}{f_2}\left(\frac{1}{[M_2]} - 1\right), \quad (13)$$

and the number of moles of effective chains per unit volume is [12]

$$n_c = C(2[M_1] + 3[M_2]) \quad (14)$$

where $[M_1]$, $[M_2]$, M_1 and M_2 are respectively the mole fractions and the molecular weights of the mono- and di-vinyl monomers, $f_2 = 4$ is the functionality of the divinyl monomer, and C is the number of moles of the divinyl monomer in unit volume of the reaction system.

With increase in the content of the divinyl monomer in the reaction system above 3 mole % the length of the effective chains becomes comparable with that of the chain of the divinyl monomer. In this case three chains—two formed by monovinyl monomer units and one divinyl monomer chain—must be regarded as meeting at a branch point. The number of effective chains in unit volume of the polymer can then be calculated from the relation [14]

$$N_c = \frac{3\rho[M_2] \cdot N_A}{(1-[M_2])M_1 + [M_2] \cdot M_2} \quad (15)$$

When the initial components have complicated compositions, the mean value M_C can be most easily calculated by choosing the most probable structure for a branch point in the polymer network, i.e. the most probable number of chains converging at one such point, and their molecular weight [16].

Approximate determination of the density of branch points in polymer networks is possible either from an analysis of the products of the controlled degradation of the polymer or from certain properties of the polymer which are related theoretically to the density of branch points. The former method involves chemical breakdown of the polymer network into linear macromolecules, which are analysed by the usual physicochemical methods [17-20]. In connection with the latter method it must be noted that theories relating the structural parameters of polymer networks to the physical properties of the polymers have been worked out only for ideal, tetrahedral networks having a low concentration of branch points.

According to the theory of rubberlike elasticity the concentration of effective chains in unit volume of an ideal network is related to the equilibrium deformation characteristics [21-23]:

$$n_c = \frac{G}{RT} = \frac{E}{3RT} = \frac{\sigma}{RT(\alpha - \alpha^{-2})} \quad (16)$$

where G is the equilibrium shear modulus, E the equilibrium modulus of elasticity under tension (compression), σ the equilibrium tensile (compressive) stress calculated on the initial cross-section of the specimen, R the universal gas constant, T the absolute temperature, and

$$\alpha = \frac{\pm\Delta l}{l_0} + 1 = \frac{l}{l_0},$$

the stretch (shrinkage) factor, in which l is the length of the deformed specimen, $\pm\Delta l$ the elongation (contraction) of the specimen, and l_0 the initial length of the specimen. According to the theory of the swelling of ideal networks in solvents or their vapours n_C is related to the equilibrium swelling by the equation [3]

$$n_c = \frac{\ln a - [\ln(1-v_2) + v_2 + \chi v_2^2]}{V^0\left(v_2^{1/3} - \frac{2}{f}v_2\right)} \quad (17)$$

where a is the activity of the solvent vapour (for the liquid $a = 1$), v the fraction by volume of polymer in the swollen specimen, χ a thermodynamic parameter of polymer–solvent interaction, V^0 the molar volume of the solvent, and f the functionality of the polymer network (the number of effective chains converging at one branch point). For polymer networks with equilibrium swelling the concentration of effective chains and the deformation properties are related by the formula [3]

$$n_c = \frac{\sigma v_2^{1/3}}{RT(\alpha - \alpha^{-2})} \quad (18)$$

A relation has been established also between the osmotic pressure P_{osm} of the equilibrium (swollen) polymer network and the concentration of effective chains therein [24]:

$$n_c = \frac{P_{osm}}{RT} \quad (19)$$

III. LAWS OF THE FORMATION OF NETWORK POLYMERS FROM POLYFUNCTIONAL MONOMERS AND OLIGOMERS

In the vast majority of cases network polymers are synthesised from complicated mixtures of polyfunctional compounds of indeterminate composition, which have been termed resins. They contain not only unchanged initial monomers but also various proportions of oligomers with different numbers of monomer units and different amounts and arrangements of functional groups or other reactive centres responsible for formation of the polymer. Since the exact composition of the resin is unknown, and is easily altered by the slightest change in the conditions of synthesis, it is impossible to predict the structural parameters of the future polymer network. Therefore the numerous studies of the formation of network polymers with resins as examples have shed little light on the laws of the formation and structure of polymer networks. Only the synthesis of polymers from individual polyfunctional compounds (monomers and oligomers) or from specified mixtures will enable sufficient experimental data to be accumulated to elucidate these rules.

1. Reactions of Polyfunctional Monomers and Oligomers in the Initial Stage

The laws governing the reactions of polyfunctional compounds in the initial stage can be assessed from the agreement between experimental results on the degree of conversion of the functional groups at the instant of gel formation and values calculated theoretically (Eqns. 1–5). The degree of conversion is easily determined by the usual methods of quantitative analysis, since the system remains soluble up to the gel point, and the reactivity of the functional groups is easily developed. The accuracy of these investigations is determined largely by the accuracy with which the instant of gel formation can be fixed in the reaction system.

According to theoretical views the point of gel formation involves an instantaneous qualitative change in the properties of the reaction mass, including an infinite increase in viscosity and the appearance of a fraction which is insoluble even in boiling solvents. Most methods of establishing the gel point have been based on fixing these changes. It has also been proposed to determine the start of gel formation from the abrupt change in the electrical [25] and dynamic mechanical [26] properties of the reaction mass. These methods are both inaccurate and

complicated experimentally. They usually require rearrangement of the apparatus to continue monitoring the formation of polymer networks after the gel point has been reached.

One of the most convenient methods for fixing the gel point is to monitor continuously the variation in the modulus of elasticity of the reaction mass by means of a torsion pendulum, in which the inertial mass is suspended by a thread comprising monofils impregnated with the test material [27-31]. This method is simple and quite accurate, and it enables formation of the polymer network to be monitored until the final stage of the reaction.

Investigations of reactions of polyfunctional compounds occurring by a step mechanism (polycondensation and step-by-step polymerisation) show that in many cases the laws of the reactions preceding gel formation are very nearly statistical [2,4,5] (see Table 1). Nevertheless, Andrianov and his coworkers have shown that, for the polycondensation of several oligomeric organic ether-acids, organic alcohols, and organometallic alcohols, variation in the number of monomer units in the oligomers causes the experimental values for the extent of reaction at the gel point to vary from that calculated statistically [32-34] (see Table 1). The start of gel formation has been found to depend on the length of the chain in the polyfunctional compounds also in the reaction of diglycidic esters with amines [35] and of several oligomeric di-isocyanates with polyfunctional alcohols [36].

Table 1. Experimental and theoretical (Eqns. 1–3) degrees of conversion of several reaction systems at the gel point.

Reaction system	r	P_{gel} expt.	P_{gel} theor.	Method of fixing gel point	Ref.
Tricarballylic acid, adipic acid, diethylene glycol	1.00 0.80	0.879 0.991	0.879 0.955	measurement of viscosity by falling sphere method	2,3
Propanediphenylene diglycidate, hydrophthalic anhydride	1.00 0.80 1.43	0.55 0.50 0.68	0.577 0.516 0.690	formation of insoluble fraction	4,5
Dimeric diglycidic ester, hydrophthalic anhydride	1.35	0.597	0.581	ditto	
Pentaerythritol tetra-adipate +					
$HO(CH_2)_2OH$	1.0	0.20	0.575	appearance of fraction insoluble in boiling solvent	32,33
$HO(CH_2)_4OH$	1.0	0.25	0.575		
$HOCH_2CH_2OCH_2CH_2OH$	1.0	0.27	0.575		
$HO(CH_2CH_2O)_2CH_2CH_2OH$	1.0	0.33	0.575		
$HO(CH_2CH_2O)_3CH_2CH_2OH$	1.0	0.35	0.575		
$O[Si(CH_3)_2CH_2OCH_2CH_2OH]_2$	1.0	0.40	0.575		
$C_6H_5Si[OSi(CH_3)_2CH_2OCH_2CH_2OH]_3$	1.0	0.36	0.41		
$Si[OSi(CH_3)_2CH_2OCH_2CH_2OH]_4$	1.0	0.23	0.33		

Discrepancies between experimental and calculated degrees of conversion of double bonds at the gel point are observed especially frequently in the polymerisation of polyvinyl derivatives or their copolymerisation with monovinyl monomers [6,37,38].

The deviations in the formation of a polymer network in the initial stages of the reaction of polyfunctional compounds probably arise from the implausibility of several postulates underlying the statistical analysis. It is difficult to suppose that under actual conditions cyclisation is completely absent, or that reactive groups maintain constant activity. Furthermore, the increase in molecular weight during the reaction is accompanied by a sharp intensification of the role of intermolecular interaction.

These deviations may become predominant with certain reaction systems or conditions, and then the reactions of polyfunctional compounds will not obey statistical laws at all. In some cases, for example, ring closure in a polyfunctional compound is energetically more advantageous than chain growth. This results in the preferential formation of cyclopolymers, with the maintenance of solubility until the limiting stages of the reactions. Such phenomena are observed in the polymerisation of divinyl derivatives in which the double bonds are separated by the number of atoms necessary for the formation of stable rings [39-41]. Similarly the polycondensation of silanetriols may lead to the formation of polycyclic or ladderlike polymers [42-45]. The reaction of anhydrides of tetracarboxylic acids with diamines, and of tetramines with dicarboxylic acids, usually yields polycyclic or ladderlike structures [46], though under certain conditions network polymers can be formed from the same components [47].

The marked departure in the laws of the reactions of polyfunctional compounds from those to be expected statistically in the initial stages may also be a consequence of differences in the activity of the reactive groups of the polyfunctional compound or of a marked change in reactivity of still unreacted groups after addition of a monomer unit to the polymer molecule [48-50]. In the limit three-dimensional structures of restricted size may be formed, dispersed in the reaction mass, the so called microgels or popcorns [48,51,52]. In this case the gel point is the instant of aggregation of the microgels by chemical combination to form a macrogel of statistically non-uniform density.

2. Polymer Networks in the Final Stage of Formation

Analysis of the degree of conversion of functional groups in the reactions of polyfunctional compounds before the start of gel formation and comparison with the theoretical values show that the development of reactions in fairly close conformity with statistical laws (formation of a uniform polymer network at the gel point) can be accompanied by marked deviations towards the preferential formation of cyclic polymers or microgel structures. The polymer structure produced in the initial stage will obviously have a decisive effect on the further course of the reaction. Thus if polymers of polycyclic or ladderlike structure are the main products in the initial stages, the reaction will develop in this direction also in its later stages, although intermolecular reactions may become increasingly probable. If, however, gel formation occurred by aggregation of microgels, further increase in density of the network of microgels with a small number of chemical bonds between them may continue beyond the gel point. In the extreme case the polymer in the final stage of the reaction will comprise densely cross-linked particles (micrograins, popcorns) distributed in an open-network matrix [51-53]. These suggestions, together with qualitative data on the non-uniform swelling of films [52,54] and the non-uniform structure observed with the electron microscope [55-67] in investigations of several network polymers, may lead to the conclusion that formation of a statistically uniform polymer network at a late stage in the conversion of polyfunctional compounds is improbable, being an exception rather than the rule [48]. However, the globular structure of network polymers mostly observed in electron-microscopic investigations is not necessarily a criterion of the microgel structure of

the polymer network. It may, for example, result from the preservation of globular structures characteristic of the chains of the initial polyfunctional oligomers or of their restoration after formation of the polymer network, similarly to what is observed with several network polymers [68,69]. These formations characterise the morphological structure of network polymers and depend, as with polymers having linear macromolecules, on the nature of the chains and the physical state of the polymer.

When investigating the laws of the formation of network polymers from polyfunctional compounds, we must first take into account the topological structure of the polymer network, which is characterised quantitatively by the concentration of effective chains. Comparison of experimental structural parameters of the network with those calculated theoretically from the composition of the reaction system and the conversion of functional groups will make it possible to elucidate details of the formation of a polymer network in the terminal stages of the reaction.

(*a*) Experimental estimation of structural parameters of polymer networks

Quantitative analysis of the conversion of functional groups is considerably more complicated in the later stages of the reaction than before the gel point. Use can be made of infrared spectroscopy [70], analysis of functional groups by conducting reactions in polymers of equilibrium swelling [5,32,70], analysis of secondary products liberated during polycondensation [71], thermal effects of the reaction [72], dilatometric analysis [73], etc. The choice of method depends mainly on the type of reactive groups involved in formation of the network polymer.

It is almost impossible to elucidate the laws of the formation of polymer networks beyond the gel point by comparing the experimental degree of conversion of the functional groups with the value calculated theoretically from the sol fraction (Eqn. 7), since the latter tends to zero long before the degree of conversion reaches 100%. At 75% conversion of the functional groups of a trifunctional monomer the theoretical sol content is already down to at most 3.5% of the weight of the reaction mass. Such a small sol fraction lies within the limits of experimental error for an extraction with boiling solvent.

Theoretical values of the structural parameters of polymer networks are calculated from the degree of conversion of the functional groups by means of Eqns. (10) and (11), or from Eqns. (12)–(15) when conversion is complete.

Experimental methods of determining density parameters of polymer networks involving their chemical degradation can be used effectively only if two types of covalent bonds differing markedly in chemical stability—weak bonds, which can be easily broken, and more stable bonds—are present in the polymer network. Examples are provided by network copolymers of unsaturated polyesters with styrene [17,18] and certain other di- and monovinyl derivatives [19], and also network polyester-urethanes [20]. Degradation methods are suitable for polymers having any concentration of chemical branch points, but they cannot take into account the effectiveness of the network chains, and they cannot be applied to the large number of network polymers having identical and stable bonds.

Methods based on theoretical relations between the structural parameters of the networks and the physical properties of the polymers (Eqns. 16–19) are the most promising and widely developed at the present time. These rules, deduced from statistical theories of rubberlike elastic deformations and the swelling of ideal tetrahedral networks with point connections and perfectly flexible chains, agree well with experimental data when the polymer contains only chemical branch points and M_C for the network considerably exceeds a segment of the polymer, i.e. in the case of open-network elastomers [3,21–23]. In the analysis of network polymers with poor chain flexibility and in the vitreous state, only the individual correlation of the experimental network parameters found under specified conditions with those calculated from the composition of the initial components and the degree of conversion of the reactive groups will enable the applicability of the method to be established and the reliability of the results to be assessed.

The applicability of the statistical theory of rubberlike elasticity to polymer networks for the experimental determination of their parameters over a wide range of concentrations of chemical branch points resulting from the reactions of polyfunctional compounds has been investigated in detail by Tobolsky and his coworkers on copolymers of vinyl monomers with oligomeric ester–maleates having a specified structure between the double bonds [12], copolymers of vinyl monomers with oligomeric ethylene dimethacrylates [12,74–78], and products of the hardening of the propanediphenylene diglycidate with various ethyleneamines [13]. The relative deviation of the structural parameters of networks from the ideal values calculated from the composition of the reaction mixture, allowing for the degree of conversion of the reactive groups and the effective participation of polyfunctional compounds in the reaction, is measured by the coefficient

$$\Phi = \frac{G}{n_0 RT} \qquad (20)$$

where n_C (in moles cm^{-3}) is the calculated density of chemical links in the network, and G the experimental equilibrium shear modulus of the network polymer in the rubberlike elastic state.

These investigations showed satisfactory agreement between theoretical and experimental network parameters for polymers whose $G-T$ curve included a horizontal section (rubberlike elasticity plateau—Fig. 1). When G is determined for temperatures 50–100 deg above the glass point of the polymer, the value of Φ varies over the range 1–3 depending on the type of network polymer (Table 2). The quantity G reaches 10^8 dyn cm^{-2} and varies little with the nature of the polymer chains. This is characteristic of polymer networks containing ten or more σ-bonds between adjacent network points (an aromatic ring is regarded as equivalent to one σ-bond). Equation (16) cannot be applied at the higher density characteristic of most dense-network polymers. The empirical equation [79]

$$\lg G = 7.0 + \frac{293\rho}{M_0} \qquad (21)$$

(where ρ is the density of the polymer at the experimental temperature), relating the density parameters of the network to the equilibrium modulus G, can be used up to the value $G = 2 \times 10^9$ dyn cm^{-2}. Fig. 2 compares the relations between G and M_C given by the theory of the rubberlike elasticity of ideal networks and by the empirical equation [21].

Kuvshinskii and his coworkers have also shown that the theory of rubber elasticity can be used to determine the network parameters of polymers obtained by the copolymerisation of several monovinyl and divinyl monomers [14].

Gul' et al. have established[80] that the theoretical relation between the equilibrium stress and moderate and small deformations (16) can be used to estimate the concentration of effective chains in the network formed by the copolymerisation of styrene with oligomeric ester-maleates. A linear relation with a correlation coefficient of 0.8–0.85 is found between the concentration of branch points determined by degradation of the copolymer with subsequent analysis of the hydrolysis products n_{chem} and the concentration calculated from the equilibrium deformation n_{phys} (with $n_{phys} < n_{chem}$ always).

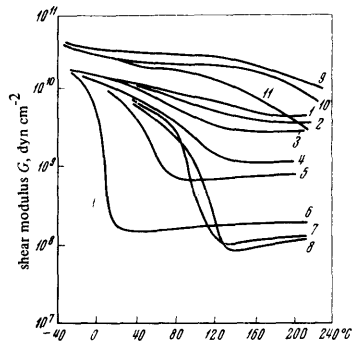


Figure 1. Temperature dependence of equilibrium shear modulus for network polymers from dimethacrylates of: 1) ethylene glycol; 2) triethylene glycol; 3) tetraethylene glycol; for network copolymers of tetraethylene glycol dimethacrylate with ethyl acrylate containing different proportions (mole %) of dimethacrylate: 4) 68; 5) 42; 6) 15.1; for network polymers from propanediphenylene diglycidate and: 7) diethylenetriamine; 8) triethylenetetramine; and for hardened resins of formaldehyde with: 9) melamine; 10) phenol; 11) urea.

Table 2. Divergence between structural parameters of polymer networks found experimentally from the equilibrium modulus of rubberlike elasticity and those calculated theoretically.

Network polymer	Equilibrium modulus G, dyn cm^{-2}	Coefficient Φ	Ref.
Сополимер стирола и тетраэтиленгликольди-			
Copolymer of styrene + 5–15 mole % of tetraethylene glycol dimethacrylate (TEGDMA)	$2.93—8.51 \cdot 10^7$	1.74—1.79	12.76
Copolymer of methyl methacrylate + 10–20 mole % (TEGDMA)	$6.67—17.2 \cdot 10^7$	1.50—1.62	
Copolymer of ethyl acrylate + 5–8 mole % (TEGDMA)	$1.37—8.93 \cdot 10^7$	0.77—1.18	
Copolymer of styrene + oligoether-maleates with mol. wt. of chain between double bonds:			
159 (70 wt.%)	$4.35 \cdot 10^8$	3.13	12
259 (20–70 wt.%)	$3.18—13.5 \cdot 10^7$	1.22—2.06	
362 (60–70 wt.%)	$2.5—2.94 \cdot 10^8$	1.99—2.79	
Polymer from propanediphenylene diglycidate + equimolecular quantity of:			
ethylenediamine	$1.43 \cdot 10^8$	1.36	
diethylenetriamine	$1.91 \cdot 10^8$	1.87	13
triethylenetetramine	$1.78 \cdot 10^8$	1.78	
tetraethylenepentamine	$1.87 \cdot 10^8$	1.88	

A fairly close correspondence between calculated (from the composition of the initial reactants) and experimental values of the modulus of rubberlike elasticity is observed also with network polymers obtained from propanediphenylene diglycidate and anhydrides of dibasic acids containing radicals of various sizes[81] (Table 3).

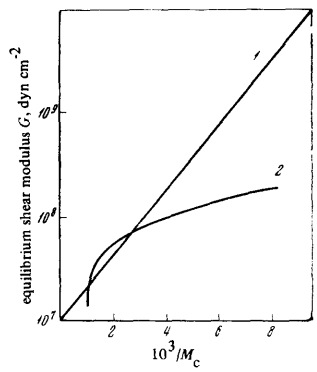


Figure 2. Dependence of equilibrium shear modulus on M_c above the glass point of network polymers from: 1) empirical equation $\lg G = 7.0 + 293\rho/M_c$; 2) kinetic theory of rubberlike elasticity $G = \rho RT/M_c$.

Quite good agreement with experimental parameters, found from the equilibrium modulus of rubberlike elasticity, is obtained for networks formed by the polymerisation of oligomeric ester-dimethacrylates with complete conversion of double bonds[82] (Table 4) if the theoretical value of M_c is taken to be not the molecular weight of the initial oligomer but its molecular weight divided by the functionality (4 in the present case).

Table 3. Calculated and experimental modulus in rubberlike elastic state of copolymers of propanediphenylene diglycidate with various anhydrides (temperature in all cases 100 deg above the glass point of the polymer)[81].

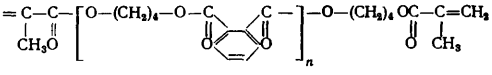
Acid anhydride	Modulus of rubberlike elasticity, dyn cm^{-2}		$\Phi = \frac{E_{exp}}{E_{calc}}$
	E_{exp}	E_{calc}	
Succinic	2.6	2.5	1.04
Methylsuccinic	1.9	2.2	0.87
Dodecylsuccinic ($C_{12}H_{23}$)	0.53	1.2	0.44
Phenylsuccinic	1.4	1.9	0.74
Maleic	3.1	2.7	1.15
Phthalic	1.9	2.2	0.87
Hexahydrophthalic	1.25	2.1	0.60

Hence the network parameters can be estimated quite accurately by determining the elastic characteristics of network polymers above their glass point. Unfortunately, there are many rigid dense-network polymers, of very great practical importance, whose glass points are above or very close to the temperature of degradation. This method cannot be applied to such polymers[12] (Fig. 1, curves *9–11*).

The relation established by Flory between the degree of swelling of polymers and the density of points in ideal

networks [3] (Eqn. 17) is of especial interest for estimating network parameters. Here the greatest experimental difficulty is encountered in determining the thermodynamic polymer–solvent interaction parameter (the Huggins constant χ). This parameter is usually determined by investigating the solubility and the properties of solutions of polymers identical in chemical composition with the network polymers [83–85]. However, especially in network polymers obtained from polyfunctional compounds, the structure of the monomer units is too diverse and is difficult to reproduce in soluble products. Furthermore, variation in the density of points in a polymer network is necessarily accompanied by a change in the chemical composition of its chains [70]. This substantial difficulty was eliminated by using solvent vapours for swelling and by linearising Eqn. (17). [86] By determining the sorption isotherm for the solvent vapour on polymers we can simultaneously determine graphically both the density of network points and the polymer–solvent interaction parameter [16,71,87]. Furthermore, determination of the degree of swelling of a polymer in the solvent vapours simplifies the experiment and improves its accuracy. Without danger of error due to extraction of the sol fraction it is possible to determine the swelling of a network polymer in the vapours of solvents over a wide range of temperatures, since at normal temperature the solvent often does not ensure destruction of physical junction points in the polymer network, and equilibrium swelling is restricted not only by chemical but also by physical junction points.

Table 4. Deviation between experimental and theoretical values of M_C for network polymers obtained from oligoester–dimethacrylates (MBP-n) [82].



Initial oligomer	Mol. wt. of oligomer	$M_{c,\,theor}$	$M_{c,\,exp}$	$\Phi = \frac{M_{c,\,theor}}{M_{c,\,exp}}$
MBP-1	446	111	85	1.30
MBP-2	666	166	160	1.02
MBP-3	886	221	280	0.78

The experimental parameter for the density of network points is, of course, higher than the theoretical value. Thus the density of branch points in a network copolymer of methyl methacrylate and methylene dimethacrylate, determined from the swelling in benzene at room temperature, is roughly ten times the value calculated from the composition of the initial mixture and supported by analysis of the degradation products of the network [88] (Table 5). Similar results have been obtained by Nielsen in an investigation of the swelling of epoxide network polymers [65].

Complete destruction of physical links in a network can be achieved by swelling the polymer in the vapour of a specially selected solvent at a certain temperature. Thus the presence of stable hydrogen bonds in networks obtained from a diglycidic ester and an oligomeric amide demands the application at an elevated temperature (70°C) of a solvent (dioxan) capable of rupturing these bonds (Table 6). Under these conditions experimental results agree with theoretical values. In the absence of stable physical links in the polymer from a diglycidic ester and an aliphatic diamine there is close agreement with theory when experiments are conducted with a non-polar solvent (dichloroethane) at low temperatures.

Table 5. Comparison of experimental estimates of concentration of chains in copolymers of methyl methacrylate with methylene dimethacrylate from degradation n_{deg} and from swelling in benzene n_{sw}. [88]

Dimethacrylate in copolymer, mole %	$10^5 n_{deg}$, moles g^{-1}	$10^5 n_{sw}$, moles g^{-1}	$\Phi = \frac{n_{sw}}{n_{deg}}$
0.201	1.61	16.0	10.0
0.509	3.56	35.7	10.0
1.04	5.61	50.6	9.2

Only acetone vapour at 50°C cleaves the hydrogen bonds in polymethylenephenols from trishydroxymethylphenol and hydroxymethyloligomethylenephenols, and the experimental values of M_C approach those calculated theoretically from the structure of the initial compounds and the degree of conversion of the hydroxymethyl groups [71,87] (Table 7). It has been found also that, on swelling in cyclohexanone vapour, only at elevated temperatures does the experimental concentration of chains approach the statistical value in the network formed by the polycondensation of phenol with formaldehyde [11].

Table 6. Structural parameters, determined under various conditions of swelling in the vapour, for network polymers from propanediphenylene diglycidate and a diamine or oligoamide [16].

Second component						
Compound	% on stoichiometric quantity	$M_{C,\,theor}$	Sorbed solvent	Sorption temp., °C	$M_{c,\,exp}$	$\Phi = \frac{M_{c,\,theor}}{M_{c,\,exp}}$
Hexamethylenediamine	100	265	chloroform	30—60	240	1.10
			dioxan	50	240	1.10
	50	492	chloroform	40—50	455	1.08
Oligoamide (Versamid)			chloroform	40	100	2.43
				50	100	2.43
				59,5	100	2.43
				35—50	110	2.20
				60	172	1.41
	75	243	dioxan	70	205	1.18
				75	205	1.18

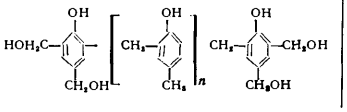
The structure of the physical links in network polymers facilitates the development of rubberlike elastic deformations and permits the use of Eqn. (18) to determine the density of chemical links alone. Table 8 shows good agreement between the parameters of network polyester–urethanes determined by this method and those calculated from the composition of the reaction mixture [89].

Thus investigation of the equilibrium swelling of polymers in solvents and especially in their vapours, and study of the deformation properties of the swollen polymers, are the most promising methods for estimating the structural parameters of polymer networks. Successive destruction of physical links by choice of solvent and the temperature of its vapour will significantly enrich our views on the role and stability of the physical links in polymer networks.

(*b*) Formation of polymer networks in the later stages of reaction

Experimental analyses of the structural parameters of polymer networks indicate that in most cases the concept of the topological structure of a network polymer as a statistical distribution in space of chains linked at points is sufficiently close to reality. In the microgel (heterophase) structure of networks it is difficult to expect such good agreement between the experimental chain concentrations found by means of physical theories of polymer networks and those calculated theoretically from the structure of the initial reactants and the degree of conversion of reactive groups. The often observed low experimental density parameters of the networks compared with the theoretical values can be explained by the presence of defects in the structure of the network at chemical links, and high values by the presence of stable physical links, which produce an apparent increase in the concentration of effective chains in the network.

Table 7. Structural parameters of network polymethylenephenols determined under various conditions of swelling in vapours [71,87].

Polymethylenephenol from:		M_c, calc	Sorbed solvent	Sorption temp., °C	M_c, exp	$\Phi = \frac{M_c, \text{calc}}{M_c, \text{exp}}$
Trishydroxymethylphenol		41	benzene	25	40	1.01
			acetone	50	55	0.75
Hydroxymethyl-oligomer	$n=1$	100	benzene	25	50	2.00
			acetone	50	95	1.05
	$n=3$	200	benzene	25	60	3.35
			acetone	50	220	0.92
	$n=5$	320	benzene	25	60	5.40
			acetone	50	380	0.84

Experimental methods of estimating structural parameters of polymer networks which involve destruction of all physical links reveal the causes of imperfection of networks which occur at chemical branch points during their formation. If the formation of network polymers in the initial stages preceding the gel point is very nearly random, the imperfection of the polymer network with respect to chemical links at a later stage in the reaction may be caused by the appearance of ineffective chains, i.e. chains attached at only one end to network points or forming closed rings (loops).

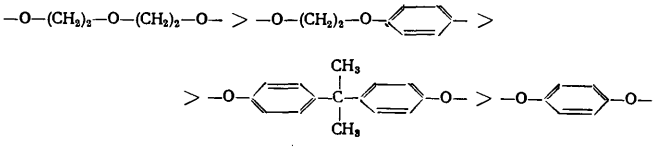
If the reactive groups are present in the central portion of the initial polyfunctional compound (of molecular weight M), even on complete conversion the proportion of the total number of chains which are ineffective is $2M_c/M$. [3,90] Hence there is no point in using polyfunctional oligomers having reactive groups near the centre if the expected value of M_c for the network is less than one-tenth of the molecular weight of the oligomer. An example of such structures is provided by polyester-maleates hardened by copolymerisation with styrene. The concentration of effective chains in them, found by physical methods, is considerably lower than the theoretical value or that found by analysis of the degradation products, if the proportion of ineffective chains in the network is disregarded [12,80].

The imperfection of a network produced by a polyfunctional compound with terminal reactive groups is determined solely by their degree of conversion and by the consumption of functional groups in the formation of rings (loops).

Table 8. Comparison of structural parameters determined from the equilibrium deformation of swollen and unswollen specimens of network polyester–urethanes formed from polyester (PE) from diethylene glycol and adipic acid ($M = 1600$) + tolylene di-isocyanate (TDI) + 1 : 1.5 mixture (A) of bis- and tris-hydroxyethylamines [89].

PE : TDI : A	M_c, calc	M_c, exp when swollen	M_c, exp when unswollen	$\frac{M_c, \text{calc}}{M_c, \text{sw}}$	$\frac{M_c, \text{sw}}{M_c, \text{unsw}}$
1:1.10:0.035	33800	33000	3700	1.02	8.90
1:1.15:0.070	24000	25000	3300	0.96	7.60
1:1.20:0.100	20000	24000	2600	0.92	9.20

In consequence of the tendency of polyfunctional compounds to cyclisation, a polymer network may not be formed at all, as already noted. If, however, a network is formed, its imperfection beyond the gel point, as a result of the consumption of functional groups in the formation of rings, should be especially marked in open networks. In some cases it has been possible to estimate the part played by ineffective groups in network polymers obtained by the copolymerisation of monovinyl derivatives with small quantities of divinyl derivatives, provided that conversion of double bonds is complete. In the copolymerisation of styrene with various divinyl derivatives, for example, the tendency to cyclisation varies with the structure of the chain in the divinyl component as follows [15]:



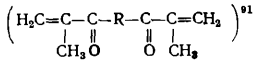
The extent to which the divinyl derivative was involved in cyclisation was estimated from the difference between the theoretical network density (from Eqn. 12) and the value found experimentally from the swelling of the copolymer in solvents (Eqn. 17). The tendency to cyclisation increases with increase in the functionality of the polyvinyl derivative [15].

Table 9 also illustrates the effect of the length and rigidity of the chain between the double bonds in the divinyl component on its ability to form ineffective loops [91]. The density of network points was calculated theoretically from the composition of the mixture and the degree of conversion of the double bonds, and was determined experimentally from measurements of the rubberlike elastic deformation of specimens in the swollen state (Eqn. 18).

The increase in network imperfection in polyether–urethanes with increase in length of the flexible chains of the oligomers, consisting of ether links [92,93], is probably also determined mainly by the formation of ineffective

loops (Tables 10 and 11). The high experimental parameters in the case of the denser networks [92] are evidently caused by a greater concentration of physical links in the form of hydrogen bonds. With increase in the density of chemical links in the polymer network it obviously becomes increasingly difficult to separate effective chains and ineffective loops, and in the case of dense-network polymers this becomes altogether impossible. The imperfection of a network formed from oligomers having terminal functional groups is then determined solely by the degree of conversion of the functional groups.

Table 9. Degree of cyclisation of dimethacrylates



on copolymerisation with styrene as a function of the structure of R. [91]

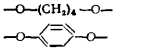
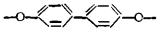
R	Cyclisation, %
—O—	52
—O—$(CH_2)_4$—O—	28
	11
	0

Table 10. Effect of molecular weight of macrodi-isocyanate (from different glycols and 3-methylpentane-1,1′,5-triol) on deviation of concentration of effective chains in the network polyurethanes from calculated values [92] (network parameters determined experimentally from equilibrium modulus of rubberlike elasticity).

Polyoxypropylene glycol		Polyoxytetraethylene glycol	
mol. wt. of di-isocyanate	$\Phi = \frac{n_{exp}}{n_{theor}}$	mol. wt. of di-isocyanate	$\Phi = \frac{n_{exp}}{n_{theor}}$
650	1.54	500	2.05
960	1.14	1000	1.06
1450	0.94	1500	0.80
1930	0.71	2000	0.57
3000	0.58	3000	0.58

Table 11. Deviation in network parameters from theoretical values for network polyurethanes (from a tri-isocyanate and a polyethylene glycol) having effective chains of different lengths [93].

Poly-ethylene glycol	$M_{c,\,theor}$	$\Phi = \frac{M_{c,\,theor}}{M_{c,\,exp}}$
Di-	351	1.29
Tri-	395	0.90
Tetra-	439	0.72
Hexa-	527	0.66
Octa-	615	0.66
Deca-	763	0.57

In complete conversion of functional groups in the terminal stage of the formation of network polymers may be due to diffusion and steric hindrances [94,95], which depend on the length and flexibility of the chains in the polyfunctional compounds and on the number and arrangement of the functional groups. Steric hindrance increases with increase in the density of network points and with intensification of the physical interaction between the network chains, i.e. with diminished probability of collision between functional groups. If at some stage the temperature of the reaction system falls below the glass point of the resulting polymer, reaction almost ceases [43,96]. In the copolymerisation of monovinyl monomers with divinyl monomers, for example, increase in the concentration of the latter makes the attainment of complete conversion of the double bonds more difficult owing to the rise in the glass point of the network copolymer, which becomes higher than the reaction temperature [43] (Fig. 3). Increase in the length and flexibility of the chain in the divinyl derivative raises the limiting degree of conversion of the double bonds. Similarly, in the formation of a network polymer from propanediphenylene diglycidate and a tetramine raising the reaction temperature above the glass point of the polymer diminishes the imperfection of the polymer network [65] (Table 12). A diminution in the functionality of the components also facilitates conversion of functional groups at the terminal stage of the synthesis of a polymer [97]. In the hardening of a diglycidic ester with acid anhydrides, increase in the bulk of the anhydride molecule, and hence increase in the steric and diffusion hindrance, increase the difference between calculated and experimental network parameters [81] (Table 3).

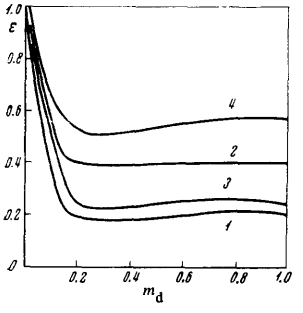


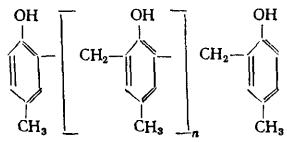
Figure 3. Dependence on their mole fraction m_d of the efficiency ϵ with which various divinyl monomers (dimethacrylates of different diols) are involved in the formation of a network polymer when copolymerised with methyl methacrylate [43]: 1) ethylene glycol; 2) decamethylene glycol; 3) 2,2-dimethylpropanediol; 4) 2-butyl-2-ethylpropanediol.

In the homopolymerisation of oligomeric ester-diacrylates it has also been established [72] that formation of the polymer network following the gel point is retarded by diffusion and steric hindrance, and the degree of conversion of the double bonds hardly ever reaches 100%. Increase in the length and flexibility of the oligomer chains facilitates attainment of the limiting degree of conversion of the double bonds.

The role of diffusion restrictions has been variously assessed in the synthesis of certain open-network polymers, especially polyether-urethanes [20,98-101].

There is a conviction that, when rigid polyfunctional molecules are used in the synthesis of network polymers, it is altogether impossible to achieve complete conversion

of functional groups owing to insuperable steric and diffusion hindrance[102]. In certain cases, however, a suitable choice of the structure of the initial reactants and of the reaction conditions may permit almost complete conversion. For example, the polycondensation of trishydroxymethylphenol proceeds until the hydroxymethyl groups have been completely converted[103] (Fig. 4). Trimeric methylenephenol containing hydroxymethyl in the terminal groups undergoes polycondensation with similar almost complete conversion of hydroxymethyl groups[71,87] to form a polymer network approximating to that calculated statistically (Table 7). With increase in the number of monomeric units in the oligomer to five and seven the proportion of hydroxymethyl groups which do not react is 33% and 38% respectively, obviously owing to steric and diffusion restrictions. The reactivity of the active hydrogen atoms in the phenolic rings of the oligomethylenecresols



drops similarly as soon as the number of units in them exceeds four[104,105]. The explanation offered[105] for this phenomenon is that the oligomers coil up owing to the presence of hydrogen bonds between the hydroxy-groups, which hinders access to the reactive groups.

Table 12. Effect of reaction temperature on structural parameters of polymer networks from propanediphenylene diglycidate and triethylenetetramine (proportions 7 : 1)[65].

Max. temp. of reaction, °C	Glass point of polymer, °C	$\Phi = \frac{M_{c,\,theor}}{M_{c,\,exp}}$
40	92	0.82
60	93	0.83
120	97	0.87

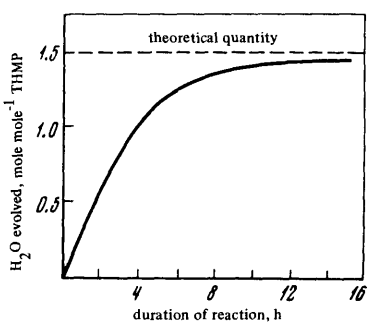


Figure 4. Kinetics of the polycondensation of trishydroxymethylphenol at 130°C.[103]

The presence, during formation of a polymer network, of a solvent or a plasticiser to promote the coiling of molecules into dense tangles increases the probability of intramolecular cyclisation and the formation of a microgel structure[20,48,77]. On the other hand, the presence of a plasticiser diminishes steric and diffusional hindrance, which allows greater conversion of functional groups and diminishes the imperfection of dense networks[78]. Long side radicals in the initial components may act as an intramolecular plasticiser[78].

Table 13. Effect of plasticiser on formation of polymer network from propanediphenylene diglycidate and triethylenetetramine in the proportions 7 : 1.[65]

Diglycidate / Plasticiser	Glass point, °C	Dynamic modulus at T_{gl} + 30 deg $10^{-7}G$, dyn cm^{-2}	M_c calc	M_c expt, from G	$\Phi = \frac{M_{c,\,theor}}{M_{c,\,exp}}$
100/0	92	8.6	305	367	0.83
90/10	84	6.8	425	411	1.04
80/20	65	4.9	544	496	1.10
70/30	60	3.9	664	580	1.14
60/40	50	3.6	783	615	1.28
50/50	26	1.5	903	1950	0.42
30/70	10	0.84	1142	3640	0.31

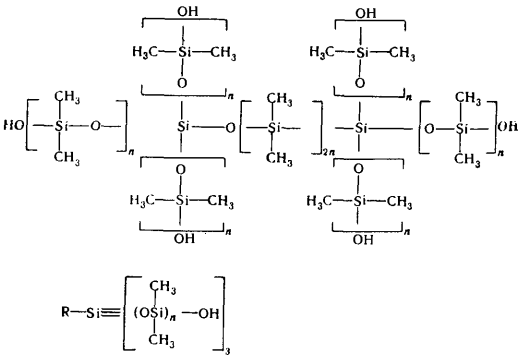
The presence in the propanediphenylene diglycidate–triethylenetetramine system of a small quantity of an active plasticiser, e.g. an oligomeric ester with a terminal carboxy-group, promotes more complete conversion of functional groups, and thus diminishes the imperfection of the network. With a high plasticiser content the tendency to cyclisation is predominant. This leads to formation of a polymer having structural parameters which differ markedly from the theoretical (Table 13).[65] Under such conditions the polymer network may have a microgranular (heterophase) structure, as is confirmed by a study of the dynamic mechanical properties of these polymers[79].

IV. CONTROLLED SYNTHESIS OF NETWORK POLYMERS

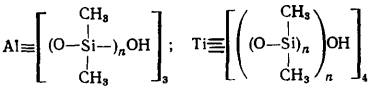
The experimental results which have accumulated on the formation of network polymers from polyfunctional compounds permit us to assess the prospects of developing syntheses of such polymers having a controlled structure. The choice of the initial compounds should obviously ensure the maximum probability of formation of a polymer network having a uniform distribution and a specified concentration of branch points, and also ensure that all monomer units are involved in effective chains. The most promising for the controlled synthesis of network polymers are oligomers containing reactive groups in the terminal units (telofunctional oligomers), since the use of oligomers having functional groups in intermediate units will result in the formation of a polymer network having a large number of ineffective terminal chains even with complete conversion of the functional groups.

The use of individual telofunctional oligomers containing two or more functional groups capable of reacting among themselves, in which the chains between the terminal units differ in nature and length, enables the structural parameters and the properties of the network polymers to be controlled within quite wide limits.

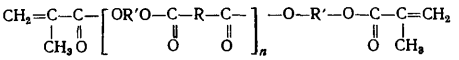
Andrianov and his coworkers have developed methods for synthesising network polymers of controlled structure



by the polycondensation of oligomeric polyfunctional organosiloxanes [106]. By regulating the value of n we can obtain network polymers which are in the vitreous or in the elastic state at room temperature. Similarly, we can obtain various network polyalumino- and polytitano-organosiloxanes



A procedure has been developed for the controlled synthesis of network polymers from oligoester–telo-acrylates



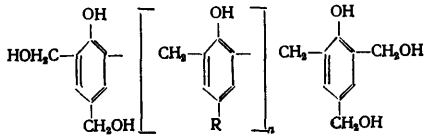
by chain polymerisation at the terminal acrylate groups [72].

Table 14. Some properties of network polyester–acrylates as functions of nature and length of oligomeric block in initial oligomers [72].

Initial oligoester-dimethylacrylate				Shrinkage on polymerisation, vol. %	Mechanical constants			
symbol	R′	R	n		hardness H_B, kgf cm^{-2}	effective modulus, kgf cm^{-2}	specific impact strength, kgf cm cm^{-2}	bending strength σ_b, kgf cm^{-2}
MDP-n	—CH$_2$—CH$_2$—O—CH$_2$—CH$_2$—		1	7.5	12.0	—	5.0	1150
			2	4.8	8.6	—	10.0	1600
			3	4.3	6.9	—	11.4	1550
			4	3.7	1.1	—	16.0	930
			5	—	0.9	—	19.0	740
MBP-n	—(CH$_2$)$_4$—		1	—	12.8	8700	3.5	845
			2	—	8.9	8650	5.7	1120
			3	—	6.4	7170	10.5	900
MBS-n	—(CH$_2$)$_4$—	—(CH$_2$)$_8$—	1	—	0.9	—	9.7	195
			2	—	0.4	—	10.2	65

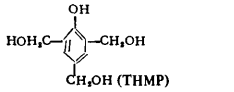
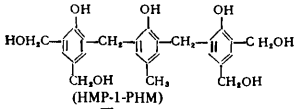
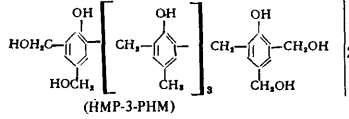
The network density is regulated by the number of ester units between the acrylate groups, and the rigidity by the structure of the radicals R and R′. The properties of network polymers from oligoester–acrylates differing in nature and size are listed in Table 14.

Network polymethylenephenols (phenol–formaldehyde polymers) of controlled structure can be obtained by the polycondensation of trishydroxymethylphenol and hydroxymethyl derivatives of oligomethylenephenols (hydroxymethyl-oligomers) having the structure [71,87]



The structural characteristics of the resulting polymer networks and several properties of the network polymers are given in Table 15.

Table 15. Properties of network products of the polycondensation of hydroxymethyl-oligomers as a function of the structural characteristics of the network [71,87].

Initial hydroxymethyl oligomer	M_c(expt.) based on		Density at 20°C, g cm^{-3}	Mechanical constants				
	chem. links	chem. and H bonds		bending modulus, kgf cm^{-2}	Rockwell hardness	specific impact strength, kgf cm cm^{-2}	compressive strength, kg cm^{-2}	δ_{bend}, kgf cm^{-2}
 (THMP)	55	40	1.300	43500	35 32—37	3.5 2.8—4.0	1100	600
 (HMP-1-PHM)	95	50	1.280	41500	32 30—33	7.5 6.7—9.2	1250	1200
 (HMP-3-PHM)	220	65	1.230	40000	30 30	9.5 8.4—10.6	1120	1650

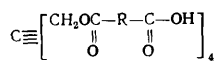
Nevertheless, the use of individual telofunctional oligomers does not always make it possible to control the density of the polymer network by varying the length of the oligomeric block without changing its nature. Variation in the length of an oligomer leads to a sharp change in the conditions for formation of the polymer network. Increase in length usually results in an increased tendency to intramolecular cyclisation of the oligomer and a decreased maximum degree of conversion of functional groups. As a consequence the imperfection of the network with respect to chemical links increases, and is difficult to control. This effect can be diminished by using binary systems for the synthesis of network polymers. They should comprise a telofunctional oligomer of a particular nature, with a definite number of units between the terminal functional groups (depending on the proposed density of network points), together with a polyfunctional compound of considerably lower molecular

weight (a hardener). The low molecular weight of the second component facilitates the achievement of limiting conversion of functional groups for almost any length of oligomer. In order to prevent the competing process of intramolecular cyclisation, it is necessary that functional groups on the same component should not interact. This method is being used increasingly to control the synthesis of open-network polymers (vulcanised rubbers). Thus the polymerisation or copolymerisation of dienes in the presence of telogens of definite structure yields rubbers of low molecular weight (polynomers) with functional groups in the terminal units, which are involved in formation of a polymer network on reaction with a vulcanising agent [90,107].

Esters containing hydroxy-groups in the terminal units, obtained by the polycondensation of dibasic acids with excess of dihydric alcohols, are used as telofunctional oligomers for the controlled synthesis of elastic open-network polyurethanes. Oligomeric ethers obtained by the polymerisation of hydroxylated rings contain similar terminal groups. The vulcanising agent can be a tri- or a tetra-isocyanate [93,108].

Oligomeric ethers and esters containing terminal alcoholic hydroxyls yield with excess of di-isocyanates oligomers, containing terminal isocyanato-groups, termed macrodi-isocyanates (precondensates). The hardeners are polyfunctional alcohols or amines of low molecular weight [89,108].

The use of such hardeners promotes more complete formation of polymer networks from oligomeric acid esters [32-34,109]



In the case of oligomeric diglycidic esters the best conditions for the production of polymer networks are provided by the use of hardeners of low molecular weight—amines or acid anhydrides [35,97].

The use of telofunctional oligomers of a specified structure to synthesise network polymers having a controlled structure permits the establishment of a relation between the network parameters and the properties of the polymers, and hence the production of polymers having specified properties. Besides the data in Tables 14 and 15 and in a review [79] there is some information on the effect of the structural parameters of networks on the properties of epoxide polymers [81,96,110,111], polyurethanes [108], copolymers of divinyl oligomers with monovinyl monomers [112,113], and several other network polymers [114]. However, it is difficult to establish an unambiguous relation between the structure of the initial oligomers and the properties of the network polymers, since the properties especially of dense-network polymers are often determined in decisive measure by other factors besides the network density. Among these are the conditions of formation of the polymers, which determine their morphological structure, shrinkages in volume resulting in the appearance of internal stresses, the test conditions, the presence of fillers, etc. Many properties of network polymers depend more on their physical state than on the density of chemical links in the polymer network. In this connection more experimental data must be accumulated on the formation of network polymers and their properties with careful control of the structure of the initial oligomers and the parameters of the resulting networks.

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Plasticisation of Polymers

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The Review surveys published information on the development of theories of the plasticisation of amorphous and crystalline polymers by plasticising additives of low and high molecular weight, the phenomenon of antiplasticisation, the action of small additions of plasticisers, and the effect of the chemical structure, size, and shape of plasticiser molecules on the plasticisation of polymers.
The applicability of modern physical and physicochemical methods (thermomechanics, thermography, rheology, nuclear magnetic resonance, infrared spectroscopy, dielectric and mechanical losses) to the investigation of plasticised systems is reviewed.
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I. INTRODUCTION

The development of effective methods for the modification of macromolecular compounds[1] is of great value for future progress in this field, and plasticisation plays an important part among these methods[2]. Indeed, polymers rarely find practical use in the individual (pure) form, owing to their brittleness, difficulty of processing into goods, tendency to crack during storage and in use, etc. Plasticisation is able not only to eliminate these defects but also to confer a new combination of valuable technical properties on the modified polymer.

The problem of the plasticisation of polymers has attracted the attention of many investigators, whose results in this field have been partly summarised in earlier reviews[3-5] and a series of papers by Soviet and foreign authors[6-13]. The present Review is devoted mainly to the part played by the chemical structure of the plasticiser in the plasticisation of polymers, blended systems, and modern methods for investigating plasticised polymers.

For a long time the problem of the plasticisation of polymers was solved exclusively by empirical methods. With the development of the science of polymers, and the expansion of knowledge of their structure, views on the nature of plasticisation also changed. The development of ideas on plasticisation can be arbitrarily divided into several stages. The first stage is characterised by a particularly empirical approach to the selection of plasticisers, the role of which was reduced merely to a lubricating effect. Then, beginning with the work of Obrist[14] (during the 1920s and 1930s), colloid-chemical concepts predominated, polymer–plasticier systems being regarded as lyophilic colloids, in which the plasticisers formed solvate sheaths on the surface of unsymmetrical particles of the polymer as the disperse phase.

However, more fundamental investigations of the nature of macromolecular compounds had already begun in the 1930s. The work of Kargin, Papkov, and Rogovin[15] showed that colloid-chemical concepts were not applicable to plasticised systems. The main kinetic laws of the behaviour of polymers during dissolution and swelling were established[16], and the heats of dissolution of vitreous polymers were studied as a function of the density of packing of the structural units.

During this period plasticisation was first interpreted as a factor diminishing the brittleness of polymers, promoting the occurrence of relaxation processes, and preventing the formation and growth of cracks under the influence of specific deforming forces[17,18]. Subsequently a quantitative relation was found between the strength of polymers and the duration of the action of deforming forces on them[19-22].

Considerable successes in studying the structure of polymers and their orientation behaviour were achieved by X-ray and electron diffraction methods[23,24]. Some part was played also by determinations of differential heats of sorption[25]. Ideas developed on the nature of the fluidity and elasticity of polymers[26,27] have remained unchanged until the present time.

It was also established[28-30] that linear polymers can exist in three physical states—vitreous, viscoelastic, and viscofluid—depending on the temperature. Two additional (intermediate) physical states—constrained-elastic and constrained-plastic—have since been established[31]; nuclear magnetic resonance has revealed[32] the existence below the glass point T_{gl} of several transition temperatures, the dependence of which on the chemical structure of the polymers has been studied.

The next stage in the development of ideas on plasticisation covered the 1940s to the early 1960s. During this period a fundamentally new approach to investigation of the plasticisation of polar and non-polar polymers was apparent especially in papers by Zhurkov and his coworkers[33-35]. Their researches enables them to formulate the now widely known rule of plasticisation—"the rule of equal mole fractions"—according to which the plasticising effect of polar plasticisers on polar polymers is the same at equal mole fractions of the former and is independent of the size, chemical nature, or structure of the plasticiser molecules. Roughly similar conclusions were reached by Fuoss[36] from a study of the plasticisation of poly(vinyl chloride), but with copolymers of vinyl chloride the laws of plasticisation were more complicated.

In a comparative study of the effect of the volume and molar concentrations of various plasticisers on the glass point of polymers, Kargin and Malinskii found[37,38] that the fall in the glass point of non-polar and weakly polar polymers conforms fairly closely to the "rule of equal

volumes" which they had deduced, according to which equal volume fractions of plasticisers produce the same plasticising effect. Since this rule and the above "rule of equal mole fractions" are obviously consequences of two different mechanisms of plasticisation, they are each obeyed only by certain systems, in which one of the mechanisms predominates, while many actual systems may exhibit larger or smaller departures from either rule [39].

Kargin and Slonimskii [40] established that small plasticiser molecules, while located between and separating the macromolecular chains, do not necessarily diminish the interaction between them, since the plasticiser itself is able to interact with macromolecular chains. They attribute the change in viscosity resulting from introduction of the plasticiser, i.e. the plasticising effect, mainly to a change in the geometrical arrangement of the molecules [40].

Energetic interaction of plasticiser molecules with certain functional groups in polymer macromolecules and the formation of a kind of molecular sorption compound have been noted qualitatively also in several other papers [41-43]. The action of plasticisers on polymers has been attributed [44] to the presence in polymer and plasticiser of groups capable of interaction, the most advantageous mutual arrangement, the shape of the plasticiser molecules, and purely geometrical factors.

A typical plasticiser is not distributed randomly in a polar polymer, since it interacts predominantly with the polar groups in the latter, blocking their force field [11]. It was established that agglomerating plasticisers significantly depress the glass point of polymers [40].

Kargin and his coworkers [45-47] showed that the rules of "equal mole fractions" and "equal volumes" applied to crystalline polymers, graft copolymers, and block copolymers.

New ideas on the structure of linear polymers, put forward by Kargin, Kitaigorodskii, and Slonimskii [48-50], provided a more accurate explanation of the nature and mechanism of plasticisation. This work opened up a new stage in the development of the theory of plasticisation.

Kargin et al. [51] studied the plasticisation of a rigid-chain polymer (cellulose) showing poor compatibility with plasticisers, and discovered two different mechanisms of plasticisation. They examined the action of plasticisers on cellulose in terms of the bundle theory of the structure of linear polymers. Plasticisation takes place within a bundle if the interaction energy of plasticiser molecules with active groups of the polymer chains is stronger than the intermolecular interaction in the polymer itself. The action of plasticisers which are completely miscible with the polymer leads to breakdown of any secondary structures. If the interaction of plasticiser molecules with the reactive groups in the polymer chains is significantly weaker than the intermolecular forces in the polymer itself, the plasticiser is able to interact only with molecules on the surface of the secondary structures: plasticisation is then accomplished only between bundles (interstructural plasticisation), without any significant change in the elastic properties of the system. Polymer materials obtained by interbundle plasticisation are characterised by great durability, high specific impact strength, and frost resistance [52,53].

Kozlov et al. [54] showed that plasticisation was possible both within and between bundles in the case of polycarbonates, which are characterised by relatively slow relaxation and crystallisation processes, and tend to form clearly developed secondary structures.

Kargin et al. [55] found that plasticisation of crystalline polystyrene produces a significant change in the conditions for formation of secondary structures characteristic of the unplasticised polymer. They note that with crystalline polymers equal fractions by volume of different plasticisers lead to the formation of spherulites of different sizes: the "rule of equal volumes" is not observed.

The new ideas on the mechanism of plasticisation are applicable, of course, also to amorphous linear polymers such as poly(vinyl chloride). [56,57] Thus the introduction of small quantities of a plasticiser into this polymer increases its degree of order [58-62]. In this case the plasticisers do not soften the polymer, but make it more rigid and brittle. The reflections on the X-ray diffraction photographs become sharpest at a plasticiser content of ~ 10 wt.%. [58,61]

With several vulcanised rubbers it has also been noted [63] that their mechanisal properties vary non-monotonically with small additions of plasticisers. This phenomenon has been explained by differences in the mobility of structural units, the stress peak at the apex of a microdefect being smoothed out.

It is possible [57] to explain the hardening of poly(vinyl chloride) by small portions of plasticisers in terms of interstructural and intrastructural plasticisation. Small additions of polar plasticisers cause interstructural plasticisation, the rigidity and strength of the polymer increasing, while the dielectric loss angle diminishes [64]; large portions of the same plasticisers, however, lead to intrastructural plasticicsation, accompanied by the opposite changes in the properties of the given polymer system. It is obvious that systems containing small proportions of plasticisers exhibit two opposite tendencies—to denser packing of chains and bundles, and to disorder under the influence of thermal motion—with the former ultimately predominating [65,66].

The variation in glass point produced by the introduction of small additions of plasticisers into crystalline polymers is oscillatory in character, as a consequence of structural changes in the polymer [67]. In several cases small additions of a plasticiser may cause the structural plasticisation of multicomponent systems, as has been demonstrated [68] for the Viniflex lacquer–tritolyl phosphate system.

Lipatov [69-71] investigated the vitrification of polystyrene and poly(methyl methacrylate), filled with glass powder and containing various quantities of a plasticiser (dimethyl phthalate), and established that the plasticisation of filled polymers is an interstructural effect, depending on the destruction of polymer–filler surface and polymer–polymer bonds.

2. PLASTICISATION AND CHEMICAL STRUCTURE OF PLASTICISERS

The above rules of plasticisation suggested by Soviet scientists played an important part in the development of ideas on the nature and mechanism of the phenomenon. The question naturally arises as to the extent to which the chemical structure of a plasticiser, or at least its homologous series, influences the plasticising effect. (The plasticising effect can be defined as the relative depression of the glass point, as the relative durability and increase in elasticity, or as the relative change in other physical properties of the polymer, under the influence of equimolecular portions of different added plasticisers.)

In the early papers of several foreign and Soviet workers [72-76] no great importance was attached to the chemical structure of plasticisers. Only the compatibility of the components, not the plasticising effect, was actively influenced by the chemical structure of polymer and plasticiser. The relative effect of plasticisers on linear polymers was regarded as depending mainly on their concentration: plasticisers having molecules of about the same size and shape exerted similar plasticising effects.

Baker [77] studied the X-ray photographs of plasticised crystalline polymers, and suggested that the original crystalline structure changes in the presence of an agglomerating plasticiser. With lubricating plasticisers an amorphous halo is merely superimposed on the phase pattern of the polymer. However, in a study of vinyl polymer–tritolyl phosphate systems, Alfrey [78] did not detect any changes in the original crystalline structure of the polymers under the influence of the plasticiser. Nevertheless, the specificity of the action of plasticisers, and the need to take chemical structure into account when selecting them, have been noted in many cases [79].

The influence of the chemical nature, size, and shape of the plasticiser molecules on the plasticisation of linear polymers by equimolecular proportions of trioctyl phosphate, tritolyl phosphate, etc. has been determined [80-82]. Plasticisers differing in the length of the hydrocarbon radicals and in molecular weight also behaved differently in compositions [83]. The effect of the chain length of the non-polar part of the plasticiser molecule on the glass point has been studied with polyvinylbutyral [84] and with other systems [85].

Experiments on synthetic rubbers showed [86,87] that with a divinylstyrene rubber the maximum plasticising effect is given by non-polar plasticisers, low contents of which satisfied the "equal volume rule" quite well. Significant deviations from this rule were observed with higher plasticiser contents, the glass point of the rubber then being lower in the presence of non-polar plasticisers than with polar plasticisers; the effect of the chemical structure of the plasticiser becomes appreciable in this case.

Many foreign scientists found that the plasticising effect depended on structural features of the plasticisers [88-90]. In particular, the mechanical properties of linear polymers were found [91] to vary with the chemical structure of the plasticiser (influence of the length of the hydrocarbon chain and of the relative content of polar groups in methacrylic esters on the plasticising effect). Here difference in chemical structure had a substantial effect on the modulus of elasticity and the strength of specimens having the same content of different plasticisers.

Polar plasticisers are usually more effective than feebly polar plasticisers towards poly(vinyl chloride). [92] The solvent power, compatibility, and effectiveness for poly(vinyl chloride) have been shown [93,99] to diminish appreciably with decrease in the relative content of polar groups in ester plasticisers.

The minimum pour point of plasticised polymers exhibited [94] a specific dependence on the structural characteristics of plasticisers having the same molecular weight: the elasticity of the polymers increased to a certain point with increase in the chain length of lateral hydrocarbon radicals in the plasticisers used—phthalic esters.

The bonds in the polymer–plasticiser system are complicated in nature [95,96], depending on their structural characteristics. It is emphasised that small quantities of different plasticisers are retained to different extents by the polymer. A point is reached at which increase in the plasticiser content does not lead to further bonding to the polymer chains. It is this portion of the plasticiser which is liable to migrate in the first instance.

Study of dielectric losses [97] and vitrification [98] in some linear polymers established that the plasticiser molecules associate with a definite number of active groups in the macromolecules depending on their chemical nature.

The role of plasticisers has been reduced [100] mainly to diminishing the steric hindrance to rotation of functional groups in macromolecular chains. The efficiency of the plasticisers is determined in considerable measure by their structure.

An electron-microscopic study [101] of the cellulose nitrate–dibutyl phthalate and cellulose nitrate–softener systems revealed that the texture of the resulting films varies substantially and depends on the solvent power of the plasticisers, i.e. on features of their structure.

The effect of chemical structure is apparent [102] both in differences in the compatibility of polymers with plasticisers, which depends on interaction energy between polymer and plasticiser molecules and on the entropy of mixing, and in differences in the plasticising effect, which depend on the shape and size of the plasticiser molecules. Poly(vinyl chloride) has been used to study the plasticising effect as a function of the structure, polarity, size, and shape of the plasticiser molecule [103,104]. With 1- and 2-naphthols the position of the functional group OH in the naphthalene molecule has been shown [105] to be important in determining the magnitude of the effect: thus 1-naphthol is a more effective plasticiser and is more compatible with this polymer than is 2-naphthol, although the polarity of the latter is the higher (the dipole moments of 1- and 2-naphthols are respectively 1.0 and 1.3 D).

The structure (degree of branching) of lateral hydrocarbon radicals in the plasticiser molecules has an appreciable influence on the plasticising effect [106]. Thus oxides of tetrahydrophthalates having branched side-chains are less effective towards poly(vinyl chloride) than are plasticisers of the same type containing linear chains. A similar effect has been observed in other systems [99].

Tager and his coworkers [107,108] used a thermomechanical method to investigate the effect of plasticisers of a new type—diphenic and naphthalic diesters and diphenic monoesters—on the glass point of polystyrene and poly(methyl methacrylate) with the same plasticiser content in the polymers. It was found that the lower the critical temperature of mixing the lower was the glass point of the plasticised polymers. As the alkyl radical in the plasticiser molecule became more bulky, the glass point first fell appreciably, and then rose. This diminution in the efficiency of the plasticisers is attributed to an unfavourable geometrical arrangement in the polymer phase of plasticiser molecules having long aliphatic radicals.

Among these compounds diphenic diesters show an outstanding plasticising effect, which is explained by the less rigid character and large set of conformations of their molecules, as a consequence of which they can be distributed among the polymer macromolecules in a large number of ways. This creates favourable conditions for better compatibility of the components and a stronger plasticising action. With naphthalic esters, which contain a rigid, planar fused-ring system, the number of possible conformations is considerably smaller, compatibility with the polymer is less, and the plasticising effect is weaker.

In the papers cited above it is concluded that the equal mole fraction and equal volume rules have limited

applicability, and that peculiarities of chemical structure must be taken into account both in selecting plasticisers and in interpreting individual facts relating to the phenomenon of plasticisation.

Considerable interest attaches to work [109] on the antiplasticisation of polymers, which is analogous to interstructural plasticisation [2]. Certain classes of organic compounds have been shown to antiplasticise polycarbonates based on bisphenols. Additions of up to 30% increase the modulus of elasticity and the strength and decrease the elongation per unit length. The depression of the glass point of the polymers is appreciably smaller than when the usual plasticisers are used.

Antiplasticiser molecules, while being polar compounds, are relatively rigid owing to the presence of cyclic structures [110]. Aromatic compounds usually exert a greater antiplasticising action than do saturated alicyclic compounds, and polycyclic compounds are more effective. Antiplasticiser molecules should also have a definite minimum size (the thickness or cross-section of such molecules should be not less than 5–5.5 Å).

An antiplasticising effect is observed [111] on the introduction into a polycarbonate of up to 15 wt.% of certain aromatic compounds containing sulphur and nitrogen, but ordinary plasticisation is observed with greater additions. Substances having a high glass point exert an appreciable antiplasticising action, but substances of lower glass point are able to plasticise the same polymers [112].

Under otherwise similar conditions the compatibility of polymers with antiplasticisers diminishes with rise in the glass point of the latter. In general antiplasticisation occurs only when polymer and antiplasticiser molecules are rigid and polar. Antiplasticisation usually improves the resistance of polymers to cracking under stress.

Antiplasticisation cannot be explained solely by crystallisation of the polymer. New bonds, detected by differential thermal analysis and by infrared spectroscopy, are formed between polar groups of the polymer and of the plasticiser. Antiplasticisation increases the density (decreases the free volume) of the polymer.

o-Tolidine as a modifying additive to poly(vinyl chloride) possesses the properties of an antiplasticiser, since it improves substantially the breaking stress under tension and diminishes the elongation per unit length [113].

Plasticisers have varied effects on the thermal stability and on the thermo-oxidative degradation of poly(vinyl chloride). [114] Oxides of hexahydrophthalates, while effectively plasticising this polymer, also stabilise it to light and to heat [115].

Maloshuk and Voyutskii [116] have shown that, in the plasticisation of the acrylonitrile copolymer SKN-40, the equal mole fraction rule is adhered to closely only by plasticisers which are of completely the same type chemically. Straight-chain and branched-chain plasticisers, as well as plasticisers of different classes, give different cohesion values.

An interesting phenomenon was discovered by Kozlov and his coworkers [117] when studying the action of mixtures of plasticisers on polystyrene. A mixture of a plasticiser of low molecular weight (phenyltributoxysilane) and an oligomeric plasticiser (polydiphenylsiloxane) gives a substantial synergic effect, and the observed displacement of glass and melting points considerably exceeds the additive values. In the plasticisation of poly(vinyl chloride) with mixtures of dibutyl phthalate (intrastructural plasticiser) and a chloroalkane (interstructural plasticiser) a transition was observed from one type of plasticisation to the other [118].

The work of various investigators, who have attempted to use the principles of the theory of interstructural and intrastructural plasticisation to make a quantitative estimate of the contribution made by the structural characteristics of plasticisers and to determine their role in the various stages of structure formation, opens up new opportunities for greater knowledge of the nature of polymers.

3. PLASTICISATION OF POLYMERS BY COMPOUNDS OF HIGH MOLECULAR WEIGHT

During recent years communications have appeared on the possibility of obtaining technically valuable polymeric compositions, which have been termed blended systems. Thus a non-volatile plasticiser—a butadiene—nitrile rubber—was suggested [119–121] for modifying thermoplastic rigid-chain polymers. A study has been made rather earlier [122] of products of the blending of SKB [a synthetic butadiene rubber] with natural rubber. Slonimskii and Komskaya [123] investigated products of the blending with one another of such rubbers as SKB, SKS-30 [a butadiene–styrene synthetic rubber], SKN-18 [a butadiene–acrylonitrile synthetic rubber], natural rubber, etc.

Study of the physicochemical nature of the phenomenon began during the same period, blending being interpreted [124–127] mainly as the plasticisation of one polymer by the other. Reznikova et al. [128] accomplished the plasticisation of poly(vinyl chloride) by butadiene–acrylonitrile synthetic rubber, studied the effect of the composition of the copolymer on compatibility and plasticising effect, and showed that the nitrile groups ensure compatibility between the copolymer and the poly(vinyl chloride), while the butadiene part exerts the actual plasticising action. Investigation of the mechanism of plasticisation established that the "mole fraction rule" was not applicable to the plasticisation of poly(vinyl chloride) by macromolecular plasticisers such as the above synthetic rubber. The limited mutual compatibility of the polymer components was also noted.

Voyutskii [102] showed that the mutual solubility of polymers is determined mainly by the change in the heat content of the system: in most cases polymers dissolve one in another only if the heat of mixing is positive. Compatibility depends also on the shape and structure of the macromolecules of the blended polymers.

Poly(vinyl chloride) can be blended in all proportions with chlorinated polyethylene [129], to give compositions of great strength, frost resistance, and good dielectric properties. Polyesters of phosphoric and cycloalkylphosphinic acids and their derivatives have also been proposed [130] as plasticisers of high molecular weight. The use of polymeric plasticisers is correctly assessed [131] as one of the most important methods for modifying polymers.

Alekseenko, Mishustin, Voyutskii, and their coworkers [132–135] undertook broad investigations of the blending of polymers. They noted the decisive role played by the polarity of the interacting components: the greater the polarity of the polymers, the greater their compatibility. In an investigation of ternary mixtures of polymers Alekseenko and Mishustin showed [136] that the plasticising action on poly(vinyl chloride) and poly(vinyl acetate) of a series of other polymers depends on the polarity of the latter. Blending requires that the polymers should be of similar polarity, and that denser packing of the macromolecular chains should be possible. However, these

workers note that the polarity of individual macromolecules may not completely balance out on blending, and the resulting system may interact with other polar polymers with the formation of ternary systems. Polar and non-polar rubbers are able to blend together [132,137] only if polar components predominate in the compositions, when the molecules of the non-polar rubber become polarised, and the polarities of the components are equalised. The possibility of blending a butadiene–vinylidene chloride rubber with rigid polymers—poly(vinyl chloride) and poly(vinyl acetate)—was also investigated [138]. The compatibility of these polymers with the rubber was assessed from the tensile strength and the elongation at rupture of films obtained by rolling followed by extrusion. A butadiene–vinylidene chloride rubber was shown to have a plasticising effect on poly(vinyl chloride); the nature of the polar groups was found to have little significance, only the polarity of the interacting substances being important.

Addition to polyethylene of the synthetic rubbers—SKB, SKS-30, DVKhB-70, SKS-30-1, SKN-18, SKN-26, SKN-40—and also polyisobutylene has been recommended to facilitate processing into articles and modification of the properties [139]. Addition of up to 25% of polyisobutylene and of the rubbers DVKhB-70 and SKS-30-1 (a ternary copolymer of butadiene, styrene, and methacrylic acid) improves the physicochemical constants of polyethylene specimens, but addition of the rubbers SKB and SKS-30 impairs its physicomechanical properties. Polyethylene blends with the above rubbers in all proportions, but does not blend with highly polar rubbers of the SKN type.

In a study of the compatibility of cellulose nitrate and poly(vinyl chloride) with several synthetic rubbers (e.g. DVKhB-70, SKN-140, SKS-30, and SKS-30-1) Alekseenko [140] observed the differing behaviour of a mixture of solutions of the polymers in a common solvent. The inadequate stability of certain mixtures with time is explained by incompatibility of the components. Mixtures of the polymer solutions may separate into layers because the energy of interaction between macromolecules of the polymers exceeds that between solvent and polymer molecules. The experiments showed that separation into layers might result also from the formation of aggregates containing the initial components in various proportions.

Polymers can be blended as latices and as aqueous dispersions; blended systems are obtained also by mixing and then extruding the finely powdered polymers; and latices or dispersions can be mixed with solutions of the polymers, and then dried and extruded [141]. Investigation of a system comprising poly(vinyl alcohol) and a carboxylated rubber showed that the latex composition considerably surpasses in mechanical properties a blended system of similar composition obtained by rolling, which is explained by a more uniform distribution of poly(vinyl alcohol) chains between the rubber globules.

In a study of the possibility of blending certain polymers Slonimskii and Struminskii [142,143] found that binary mixtures of equally concentrated solutions of polybutadiene and a butadiene–styrene copolymer, natural rubber and polystyrene, separate into two phases, although the heat of mixing of the polymers is positive. This anomaly was explained by change in the packing density of molecules of the initial polymers on mixing.

Lel'chuk and Sedlis [144] studied the compatibility of macromolecular substances with the aim of determining the possibility of plasticising poly(vinyl chloride) with polymeric plasticisers. Plasticising power was measured by the depression of the glass point of the composition compared with that of the unplasticised polymer. butadiene–nitrile rubber containing 35–40% of acrylonitrile showed the best compatibility and efficiency.

Berlin, Kargin, and their coworkers [145,146] examined the blended systems formed by poly(vinyl chloride) with methylvinylpyridine rubber (SK MVP) and with nitrile rubber SKN, and showed that a certain schedule of treating the mixtures on rolls yields graft copolymers by chemical interaction between functional groups of the poly(vinyl chloride) and those of the rubbers. With SK MVP rubber as modifier cross-links of the pyridinium type are formed, and with SKN *N*-substituted nitrilium salts may be formed. Addition of small quantities (5–10%) of the above modifiers produces a sharp improvement in the stability of poly(vinyl chloride) to impact loads.

Slonimskii et al. [147] investigated the mechanical properties of polymer mixtures, and showed in particular that the X-ray photographs of mixtures of crystalline and amorphous polypropylene and polyisobutylene confirmed the incompatibility of the components: the mixtures are two-phase colloidal systems. Addition of an amorphous component diminishes the strength of polypropylene and prevents development of the high stresses necessary for the production of constrained viscoelastic deformations, so that the elongation of the specimens on rupture is decreased. It was shown also that mixtures of crystalline polymers, e.g. polypropylene and polyethylene, exhibit microheterogeneity. A similar situation can be observed with a mixture of polypropylene and polyisobutylene.

Polytetrafluoroethylene possesses superior physicomechanical and dielectric properties and great chemical stability. However, it cannot be fabricated into articles by injection moulding, extrusion, hot pressing, etc., but requires special, laborious procedures. Numerous attempts to improve the workability of polytetrafluoroethylene by adding small quantities of greases, fillers, polyisobutylene, etc. have not yielded practical results.

The possibility of modifying polytetrafluoroethylene with high-density and low-density polyethylene has been studied [148,149]. After careful grinding and mixing, the polymers were blended in the solid phase by pressing or on rolls at 150–155°C. With increase in the polyethylene content the breaking stress on stretching increased substantially, the optimum content being 30 to 50%. It is interesting that, whatever the proportions of the components, blended systems of this type give X-ray photographs characteristic of the original crystalline polymers. Differential thermal analysis has established [150] that the melting ranges in the blended systems coincide with those of pure polyethylene and pure polytetrafluoroethylene. This indicates that this blended system is formed not by chemical interaction, with the formation of some new chemical compound like a block copolymer, but by secondary intermolecular bonds between the chains of the initial polymers, without change in their original crystalline structure. The above compositions constitute an example of polymer systems in which the introduction of a macromolecular modifier (polyethylene in the present case) results not in a weakening but in a strengthening of intermolecular interaction.

Experiments by several workers [144] on the blending of poly(vinyl chloride) with various brands of nitrile rubbers also confirmed that up to 150–160°C the latter act as plasticising additives in the compositions. Blended systems have been obtained from polyethylene, polystyrene, DVKhB rubber, and other polymers [151].

Dogadkin et al. [152,153] showed that polymer mixtures of optimum composition improve the resistance of vulcanised rubbers to fatigue on repeated deformation, in comparison

with those based on the individual rubbers. In mixed systems the disintegration of specimens subjected to repeated deformations also begins with the growth of microcracks formed at the site of some structural defect. However, a microcrack arising in a medium of lower modulus of elasticity slows down or ceases its further growth on meeting a rubber particle of higher modulus, owing to the possibility of stress relaxation at the apex of the crack. If, on the other hand, the microcrack arises in a medium of higher modulus of elasticity, the overstresses at the apex of the growing crack readily relax on encountering particles of a disperse phase having greater pliability.

In most cases blended systems do not form true solutions [154]: i.e. they are not thermodynamically compatible. Hence they are microheterogeneous (heterophase).

Most blended systems can be regarded as a kind of plasticised system [155] primarily because, as with ordinary plasticisation, the polymeric component of the mixture having the more rigid chains shows some depression of its glass point, increase in deformability, and decrease in the strength of the material, although all these effects are less strongly developed than with agglomerating plasticisers of low molecular weight.

Zelenev and Bartenev [156] studied the relaxation properties of mixtures of polar and non-polar rubberlike polymers over a wide temperature range. They showed that, with non-compatible rubbers (SKS-30 and SKN-26) below the glass point, no significant changes occur in the properties relative to those of the pure rubbers, whereas in the case of a mixture of compatible rubbers (SKS-30 and natural rubber) the low-temperature maximum of mechanical losses diminishes and moves to higher temperatures. Mechanical losses and X-ray diffraction have been used [157] to investigate the relaxation properties of some heterogeneous polymer compositions based on a crystallising isoprene rubber SKI-3 blended with a partly crystalline polymer (isotactic polypropylene), and to establish that polypropylene causes the formation of ordered structures: i.e. it is a structure-forming agent.

It has been shown [158] that butadiene–nitrile rubber (SKN-40) has a considerable plasticising effect on cellulose acetate–butyrate, which conforms to the equal-volume rule and is molecular in character.

The chemical structure of the plasticising components obviously plays a considerable part in the plasticisation of polymers by macromolecular substances. Furthermore, the re-formation of supermolecular secondary structures on contact of a polymer with another, plasticising polymer probably occurs differently from in the presence of a plasticiser of low molecular weight.

It must be remarked that, on the whole, blended systems have not yet been studied at all adequately, and many interesting theoretical and practical papers may be expected to appear in this field in the near future. Thus ternary systems, consisting of two polymers and an antiplasticiser, which increase significantly the strength of blended systems while maintaining all other performance figures, may be of great interest [151].

4. MODERN METHODS OF INVESTIGATING PLASTICISED SYSTEMS

The thermomechanical method proposed by Kargin and Sogolova [159], and subsequently modernised by Teitel'baum [160], has been of great value in studying the mechanism of the plasticisation of polymers at all stages. Thermomechanical curves can be obtained in principle by use not only of compressive forces [161] but also of stretching [162], bending, twisting, etc. forces. The thermomechanical method is interpreted [163] as recording creep (the gradual accumulation of deformation) with a constant load and a gradual rise in temperature at a constant rate. Such regularities in plasticisation as the equal mole fraction and equal volume rules, and to a considerable extent the laws of interstructural and intrastructural plasticisation, were discovered by the successful application of the principles of the thermomechanical method of investigation [164].

The thermomechanical method has been used [165] to study the plasticisation of polymers undergoing crystallisation (cellulose triacetates). Plasticisers (butyl stearate and tritolyl phosphate) depress the glass point, but, because of the crystallisation of the polymer, the plateau of rubberlike elasticity on the thermomechanical curves is located below that for the pure polymer: i.e. the deformability is not increased but is diminished.

Infrared spectroscopy has been widely used to investigate the structure and properties of individual macromolecular compounds [166,167]. It enables us to assess the nature of the forces of intermolecular interaction between certain groups in the polymer chains and the plasticiser, as was first demonstrated by Zhurkov and Levin [168].

An investigation was made by infrared spectroscopy [169] of the interaction between poly(vinyl chloride) and an antiplasticising additive (*o*-tolidine). The appearance in the absorption spectrum of the composition of a band at 3200 cm^{-1} indicates the formation of a hydrogen bond between the amino-group and the polar CHCl group of the polymer. Hydrogen bonding in this case may explain the significant hardening of the polymer on being blended with *o*-tolidine. However, the number of papers on the application of infrared spectroscopy to investigate the plasticisation of polymers is extremely small.

The thermographic method is of great value for investigating plasticised systems, and is quite widely used at the present time to study [170] individual macromolecular compounds. Mikhailov et al. [127] studied the polyethylene–polypropylene system by this method, and showed that blending is observed at quite definite proportions of the components, one of which (polyethylene in the present case) is a plasticiser for the other.

Under the influence of polar agglomerating plasticisers the positions on the differential thermal analysis curves of the effects due to vitrification and breakdown of the crystalline phase are displaced to lower temperatures in the intrastructural plasticisation of poly(vinyl chloride) [171]. At certain temperatures modifying additives (*o*-tolidine, 4,4′-dinitrobiphenyl, etc.) containing active functional groups NH_2 and NO_2 were found to interact chemically with the CHCl groups of the polymer. Thermography also reveals the change in the endothermicity of pyrolysis of the polymer produced by plasticisers, which permits monitoring of the effect of water of crystallisation and other forms of moisture on the course of plasticisation [172].

Thermographic investigation [173,174] of the plasticisation of poly(vinyl chloride) with anthracene, anthraquinone, and *p*-terphenyl showed that anthraquinone displaced the endothermic effects on the differential thermal analysis curves to higher temperatures, whereas the other two compounds produced a shift to lower temperatures. Thus this method of investigation enables us to assess the effectiveness of plasticisers with a given polymer. At the same time cases can be observed of depression of the crystallisation point of plasticisers under the influence

of a polar polymer, and the presence of a small amount of crystalline phase can be recorded in such a polymer as suspended poly(vinyl chloride).

A thermographic study has been made [175] of the effect of plasticisers on transition temperatures in poly(vinyl chloride). This method can also be used [176] to study transformations in blended systems, e.g. a poly(vinyl chloride)—butadiene–acrylonitrile elastomer.

Nuclear magnetic resonance, which enables the mobility of molecules as a whole, of groups, and of atoms to be studied directly, has also acquired great value for investigating individual polymers [177] and plasticised systems [178]. When applied to plasticised polymers this method may yield information on the molecular motion of the plasticiser in the polymer phase, which has been studied [179] for plasticised polystyrene.

The efficiency of plasticisers can be determined by measurement of the spin–spin and spin–lattice relaxation times T_2 and T_1. [180] The influence of the chemical structure of plasticisers on their efficiency can also be followed in these nuclear magnetic resonance experiments. The method enables the type of plasticisation (intrastructural, interstructural, or mixed) to be established [181] for a given polymer, e.g. poly(vinyl chloride), by determining the concentration dependence of the dimensionless quantity T_2/T_1^0, which may serve to characterise the interaction between polymer macromolecules and the plasticiser.

The dielectric loss method [182,183] provides an efficient means for revealing the relation between the properties of polymer systems and their molecular structure. It has been used to study molecular relaxation over wide ranges of temperature and frequency in the rubberlike elastic state of pure and plasticised polymers [184,185], and to calculate relaxation times, the form of their distribution, and correlation factors in the expression for the effective dipole moment [186,187]. These parameters are sensitive to the molecular structure both of the polymers themselves and of plasticising additives present in them. The dielectric loss method can also be used to study [188-191] the influence of the chemical nature and structure of plasticisers on the plasticising effect as shown by the dielectric characteristics of the polymers.

The dielectric loss method has been used to establish [192,193] the dependence of the plasticising effect with poly(vinyl chloride) on the size and shape of the plasticiser molecules, the type, number, and position of functional groups and of benzene rings, and also the displacement of the temperature of maximum tan δ relative to the pure polymer.

Rheological investigations of polymer–plasticiser systems are acquiring great value, providing a basis for processing schedules, and establishing the structure of the melt and certain physical properties of plasticised systems [194-200].

Viscometry has been used [201] to investigate the interaction of poly(vinyl chloride) with plasticisers as a function of the nature of the latter. Viscosity and the points at which swelling, gel formation, and dissolution of the polymer start show an extremal dependence on the type of plasticiser.

The resonance method [202] (determination of the dynamic mechanical characteristics) is of great interest for the investigation of plasticised systems. Zelenev and Bartenev [203] studied the effect of plasticisation (with dibutyl phosphate, dioctyl sebacate, and dibutyl sebacate) on the relaxation properties (mechanical losses) of polar and non-polar rubberlike polymers over a wide temperature range. At high temperatures plasticisers are more effective with non-polar rubbers, and at low temperatures with polar rubbers. The action of plasticisers has different mechanisms in the regions of the main, low-temperature, and high-temperature mechanical-loss maxima. In each case there are differences with polar and with non-polar rubbers. Study of vulcanised filled mixtures of polar and non-polar rubbers has shown [204] that the combination of dynamic mechanical with physicomechanical measurements gives a fairly complete idea of the character and properties of compositions based on mixtures of rubbers, in particular on their degree of microheterogeneity.

The resonance method enables us to trace [205] the dependence of the velocity of sound on the composition of the mixture and the glass and pour points. Its use reveals the ordering and denser packing of poly(vinyl chloride) macromolecules at low concentrations of a plasticiser of high molecular weight, and also the increase in the velocity of sound and in the strength of poly(vinyl chloride) with increase in the SKN-40 content [206].

In several cases plasticisation itself can be used as a method for studying the structure and other properties of polymers [207]. By varying the plasticiser content in poly(vinyl chloride) in suspension and in a latex, for example, a transition in structure can be observed. At plasticiser concentrations below 50% the supermolecular secondary structures of the polymer form a fibrillar network immersed in a continuous liquid phase. At higher concentrations the structure consists of fibrils which have coalesced to enclose droplike inclusions. This leads to an anomalous variation not only in strength but also in electrical conductivity, permeability to gases, and several other properties.

Plasticisation has been used [208] to study the variation in the strength of poly(vinyl chloride) with time. Interstructural (interbundle) plasticisation with small amounts of plasticisers is found to increase the durability of poly(vinyl chloride)–plasticiser systems.

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Despite definite advances in the plasticisation of polymers and methods of investigation, several important and complicated problems, in our view, face this branch of science and technology, including

(*a*) development of a unified theory of plasticisation, which will enable the type of plasticiser having a definite plasticising effect to be selected for each type of polymer from the chemical structure of the interacting component;

(*b*) study of the part played by different types of plasticisers at separate stages in the formation of supermolecular secondary structures during polymerisation and processing, which will predetermine a combination of physical properties of the polymers [209];

(*c*) research into the possibility of obtaining synergic effects in the action of mixtures of plasticisers for a wide range of polymers;

(*d*) separation and application of general-purpose plasticisers combining several functions—like e.g. oxides of tetrahydrophthalates [106], which are not only efficient plasticisers but also good stabilisers for poly(vinyl chloride); and

(*e*) further study of the plasticisation of network polymers, the plasticisation of polymers by macromolecular compounds [210,211], and the formation of blended systems by mixing latices and aqueous dispersions of polymers [212,213].

Successful solution of this far from complete list of problems will permit a substantial broadening of our views on the phenomenon of plasticisation and improvement in the technical standard of the production and application of plasticised polymeric materials.

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General Theory of Separation and Chromatography

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The fundamental characteristics of the operation of chromatographic columns have been discussed from the standpoints of the general theory of separation; relations applicable in principle to any method of the chromatographic separation of binary mixtures, regardless of the nature and magnitude of the elementary separation step on which it is based, are presented. The bibliography includes 34 references.

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I. INTRODUCTION

In connection with the elaboration[1] and development[2-5] of the circulation chromatographic method whereby it is possible to employ repeatedly the same stationary sorbent bed for the separation of a binary mixture, there arose the necessity to compare it with other processes involving the separation of binary mixtures in columns (distillation, thermal diffusion, centrifuging, etc.). At first sight, the concept of theoretical plates developed in a number of studies[6-8] might serve for this purpose. However, in chromatography the theoretical plate bears no relation[9] to the concept of the theoretical separation stage in the general theory of separation[10].

Comparatively recently the concept of an ideal cascade in chromatography was developed[11]. This involved the introduction of the idea of the height equivalent to the theoretical stage (HETS), which is equivalent to the analogous idea employed earlier for a chromatographic column with complete (special) phase reversal at the ends of the separation zone[12,13]. However, when formulating a specific problem—the comparison of various versions of the continuous circulation-type separation of binary mixtures—the relation between the general theory of separation and chromatography was inadequately elucidated and was limited essentially to the discovery of an analogy between partition in terms of relative concentrations in the chromatographic column and in an ideal fine-separation cascade.

In order to reflect more completely the existing relation, a parallelism is drawn here between chromatographic separation processes and liquid extraction processes, on the basis of which a clearer definition of HETS in chromatography is given together with its relation to the height equivalent to a theoretical plate (HETP) and the optimum conditions for chromatographic separation are discussed. An analogy is also drawn between the operation of a chromatographic column with full phase reversal and a rectangular fine-separation cascade and certain new methods of gas-chromatographic separation are discussed.

II. ANALOGY BETWEEN LIQUID EXTRACTION AND CHROMATOGRAPHY IN THE LIGHT OF THE GENERAL THEORY OF SEPARATION

In the study of chromatographic separation processes an analogy is often drawn between them and liquid extraction processes. This analogy has in fact led to the development of the concept of the theoretical plate in chromatography. The chromatographic column is regarded as consisting of individual elements (plates). Equilibrium must be attained in each such element, i.e. the process takes place as follows: initially the substance enters the first element where equilibrium is established, then the same thing occurs in the second element and in the next, etc., i.e. the real process is imagined to take place on the pattern of the processes occurring in Craig apparatuses[14-16].

In the present section the analogy between liquid extraction and chromatography will also be employed for the further development of the concept of the ideal cascade in chromatography.

1. Ideal Liquid-Extraction Cascade

We shall analyse the operation of a separation apparatus the three stages of which are shown in Fig. 1. The apparatus is a cascade consisting of N series-connected theoretical separation stages. Here the theoretical or ideal stage is understood, as usual[17], as a stage in which the duration of the interaction between the phases is sufficient for the attainment of equilibrium characterised by the elementary separation step. Thus the extract and the material leaving the theoretical stage are solutions in thermodynamic equilibrium with one another.

We shall restrict the treatment to the case of immiscible extractants and to extraction with independent partition of the components (which is frequently observed for dilute solutions, particularly when the partitioned components are undissociated substances or substances which do not react

with any components of the extractant[17]). One of the separation stages in this cascade is shown in Fig. 2 with an indication of the streams and the corresponding concentrations. The separation stage has the following characteristics: a feed flux L at a concentration x enters it with two fluxes emerging at the other end—one partially enriched in the component extracted (L', x') and the other partially depleted in the component (L'', x''). In the case of extraction

$$L' = \varkappa u c_1 + \varkappa u c_2 = \varkappa u c_0 , \quad (1)$$

$$L'' = \varkappa_1 v a_1 + \varkappa_1 v a_2 = \varkappa_1 v a_0 . \quad (2)$$

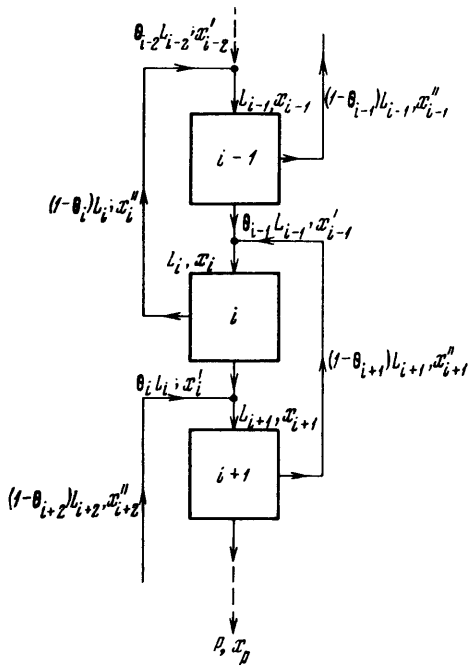

Figure 1. The cascade.

Here u and v are the linear velocities of the extractants, $\varkappa$ and $\varkappa_1$ are the fractions of the cross-section of the stage occupied by the extractants, c_1 and c_2 are the amounts of the first and second components of the mixture to be separated in the first extractant, and a_1 and a_2 are the amounts of the first and second components in the second extractant.

Bearing in mind that

$$L = L' + L'' , \quad (3)$$

we obtain

$$L = \varkappa u (c_0 + \lambda a_0) , \quad (4)$$

where

$$\lambda = \frac{\varkappa_1 v}{\varkappa u} \quad (5)$$

is the ratio of the extractant fluxes.

Then

$$x' = \frac{c_1}{c_1 + c_2} = \frac{c_1}{c_0} , \quad (6)$$

$$x'' = \frac{a_1}{a_1 + a_2} = \frac{a_1}{a_0} . \quad (7)$$

Since

$$Lx = L'x' + L''x'' \quad (8)$$

by substituting Eqns. (1), (2), (4), (6) and (7) in Eqn. (8), we obtain

$$x = \frac{c_1 + \lambda a_1}{c_0 + \lambda a_0} . \quad (9)$$

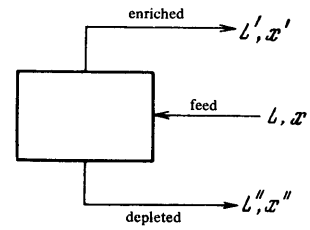

Figure 2. A stage in the cascade.

The relative concentrations[18] will be correspondingly defined by the following equations:

$$\xi' = \frac{x'}{1 - x'} = \frac{c_1}{c_2} , \quad (10)$$

$$\xi'' = \frac{x''}{1 - x''} = \frac{a_1}{a_2} , \quad (11)$$

$$\xi = \frac{x}{1 - x} = \frac{c_1 + \lambda a_1}{c_2 + \lambda a_2} . \quad (12)$$

Introducing the ratio of the enriched fraction to the feed flux (the degree of separation[18]), we obtain

$$\theta = \frac{L'}{L} = \frac{c_0}{c_0 + \lambda a_0} . \quad (13)$$

The degree of separation attained in one stage is called[18] the separation factor α. The latter is defined as the ratio of the relative concentration in the enriched fraction to the relevant concentration in the depleted flux:

$$\alpha = \frac{\xi'}{\xi''} = \frac{a_2}{a_1} \cdot \frac{c_1}{c_2} = \frac{k_2}{k_1} , \quad (14)$$

where k_1 and k_2 are partition coefficients.

Another measure of the degree of separation achieved in the stage is the effective separation factor[18] β:

$$\beta = \frac{\xi'}{\xi} = \frac{1 + \lambda k_2}{1 + \lambda k_1} . \quad (15)$$

Hence

$$\lambda = \frac{\beta - 1}{k_2 - \beta k_1} . \quad (16)$$

It is known[17] that in the separation of components by liquid extraction best results are achieved when the volume ratio of the phases corresponds to symmetrical separation:

$$\lambda_0 = \frac{1}{\sqrt{k_2 k_1}} . \quad (17)$$

We shall attempt to explain this result from the standpoint of the general theory of separation. For this purpose, the principle of the rationality of the cascade formulated previously[19,20] will be employed.

In principle, the role of each stage and of the entire separation cascade consists in the separation of the mixture components. In terms of thermodynamics, this means that under all conditions the operation of the cascade and all its elements consists in a decrease of the entropy (of mixing) of the system. Hence a cascade operating without mixing in any of its units fractions with different concentrations of the component to be extracted must evidently be regarded as thermodynamically the most effective (ideal).

Fig. 1 shows that each stage of the cascade is fed by two fluxes: by the enriched flux from the upper adjacent stage and by the depleted fraction from the lower stage. Only in these units is there a possibility of the mixing of fractions and consequently it is in fact here that particular care should be taken to avoid an increase of entropy.

Thus according to the principle of the ideality of the cascade,

$$\ldots\ ;\ x''_{i+2} = x'_i;\ x''_{i+1} = x'_{i-1};\ x''_i = x'_{i-2};\ \ldots \tag{18}$$

and consequently

$$\ldots\ ;\ x_{i+1} = x'_i;\ x_i = x'_{i-1};\ x_{i-1} = x'_{i-2};\ \ldots \tag{19}$$

Conditions (18) and (19) can also be expressed in terms of relative concentrations:

$$\xi''_{i+1} = \xi'_{i-1} = \xi_i\ . \tag{20}$$

By definition of the effective separation factor,

$$\xi'_i = \beta\xi_i\ . \tag{21}$$

According to Eqn. (20), for an ideal cascade,

$$\xi'_i = \beta\xi''_{i+1} \tag{22}$$

and

$$\xi'_{i+1} = \beta\xi'_i\ . \tag{23}$$

Multiplying together the last two equations, we obtain

$$\xi'_{i+1} = \beta^2\xi''_{i+1}\ , \tag{24}$$

but, by definition of the separation factor,

$$\xi'_{i+1} = \alpha\xi''_{i+1}\ , \tag{25}$$

so that

$$\beta = \sqrt{\alpha}\ . \tag{26}$$

This relation between the effective and thermodynamic separation factors is[10,18-20] the fundamental property of the ideal cascade.

Using Eqns. (14), (15) and (26), it is easy to show that condition (17) is identical with the fundamental property of the ideal cascade and is thus a necessary and sufficient condition for its determination.

For the practically important case of fine separation[10,18-20] where $\alpha - 1 \ll 1$, the geometrical mean may be replaced by the arithmetical mean. Then

$$\lambda_0 \simeq \frac{2}{k_1 + k_2}\ . \tag{27}$$

The resulting equation is identical with the equation derived previously[21] in the calculation of the optimum ratio of the carrier fluxes in a countercurrent chromatographic column and can thus serve as additional confirmation of the validity of the concept of the ideal cascade in chromatography.

It is useful to note that so far in the general theory of separation only one type of ideal cascade has been considered—the continuous-operation ideal cascade characterised by a maximum[10,18,19] on the overall flux distribution curve, the positions of which coincides with the feed point. However, according to the literature data[17], condition (17) is valid not only for a liquid extraction cascade with continuous feed but also for fractional extraction in a Craig apparatus[17], where the distribution of the component fluxes is Gaussian[17,22]. On this basis, one may consider two types of ideal cascade differing in the specific distribution of the component fluxes.

It is possible to show that the overall degree of separation q_0 achieved by the ideal cascade is defined[10] by an equation of the following form:

$$q_0 = \frac{\xi_N}{\xi_0} = \alpha^{N/2}\ . \tag{28}$$

For the case of fine separation we have correspondingly

$$\xi_N = \xi_0\ e^{N/2\cdot(\alpha-1)}\ , \tag{29}$$

where ξ_0 is the relative concentration at the feed point.

On the basis of the above equations, one can imagine how the transition from the second type of ideal cascade to the first may occur. Indeed, we can find the changes which will occur when, during the separation of a binary mixture, the latter is continuously introduced at the feed point. If the condition of extraction with independent partition of components is not thereby violated, the relative concentration partition law should hold, so that continuous introduction of the mixture may be regarded as an infinite number of pulse injections of the mixture at the feed point, which leads to a superposition of a large number of Gaussian distribution curves[11].

2. HETS in Chromatography

HETS in chromatography may be determined from a consideration of the chromatographic zone for a binary mixture. Fig. 3 shows that

$$A'_1 = A_{\max_1}\exp\left[-\frac{(s'_1)^2}{4D^*_1 t}\right]\ , \tag{30}$$

$$A_{0,1} = A_{\max_1}\exp\left[-\frac{(s^0_1)^2}{4D^*_2 t}\right]\ , \tag{31}$$

where

$$s'_1 = \pm\,(l - s^0_1)\ , \tag{32}$$

$$D^*_1 = \frac{D_{\mathrm{eff}_1}\varkappa}{\Gamma_1}\ , \tag{33}$$

$$A_1 = c_1\Gamma_1\ , \tag{34}$$

$$\Gamma_1 = \varkappa\left(1 + \frac{\varkappa_1}{\varkappa}k\right) = \varkappa(1 + k'_1)\ , \tag{35}$$

and D_{eff_1} is the effective diffusion coefficient[22,23].

After dividing Eqn. (30) by Eqn. (31) and using Eqn. (32), we obtain

$$\ln\frac{A'_1}{A_{0,1}} = \frac{l}{4D^*_1 t}[2s^0_1 - l]\ . \tag{36}$$

For the second component

$$A'_2 = A_{\max_2}\exp\left[-\frac{(s'_2)^2}{4D^*_2 t}\right]\ , \tag{37}$$

$$A_{0,2} = A_{\max 2}\exp\left[-\frac{(s_2^0)^2}{4D_2^* t}\right], \quad (38)$$

where

$$s_2^l = s_2^0 + l . \quad (39)$$

Having divided Eqn. (37) by Eqn. (38) and using Eqn. (39), we have

$$\ln\frac{A_2^l}{A_{0,2}} = -\frac{l}{4D_2^* t}[2s_2^0 + l] . \quad (40)$$

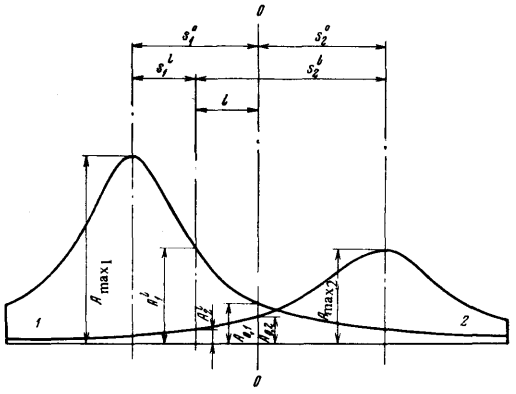

Figure 3. A chromatographic band.

By combining Eqns. (36) and (40) and putting $D_1^* = D_2^*$, we obtain

$$\ln q_0 = \frac{l(s_1^0 + s_2^0)}{2D^* t} . \quad (41)$$

The values of s_1^0 and s_2^0 may be found using the equation derived previously[11,21] for the calculation of the velocities of the chromatographic zones in a system of coordinates linked to the feed cross-section of the chromatographic band:

$$v_{s_1} = \frac{s_1^0}{t} = \frac{u(1-\lambda_0 k_1)}{1+k_1'} , \quad (42)$$

$$v_{s_2} = \frac{s_2^0}{t} = \frac{u(1-\lambda_0 k_2)}{1+k_2'} . \quad (43)$$

From the condition

$$v_{s_2} = -v_{s_1} , \quad (44)$$

we obtain

$$\lambda_0 = \frac{\tilde{\alpha}+1}{k_2 + \tilde{\alpha}k_1} , \quad (45)$$

where

$$\tilde{\alpha} = \frac{\Gamma_2}{\Gamma_1} . \quad (46)$$

On substituting Eqn. (45) in Eqns. (42) and (43), we obtain

$$|s_1^0| = |s_2^0| = \frac{\varkappa u}{\Gamma_1}\frac{\alpha-1}{\alpha+\tilde{\alpha}} \cdot t , \quad (47)$$

whence

$$\ln q_0 = \frac{l}{\frac{D_{\text{eff}_1}}{u}} \cdot \frac{\alpha-1}{\alpha+\tilde{\alpha}} . \quad (48)$$

The application of the concept of HETS to columns is known[10,17] to be useful only in the separation of isotopes where $\alpha - 1 \ll 1$. In the separation of the usual mixtures, the best characteristic is the height per unit transfer[10,17] (HET), since with a correct choice of the determining phase, HET is independent of α, in contrast to HETS.

Taking this into account, we can transform Eqn. (48) for the case of $\alpha - 1 \ll 1$, obtaining

$$\ln q_0 \simeq \frac{l}{\frac{D_{\text{eff}}}{u}} \cdot \frac{\alpha-1}{2} . \quad (49)$$

We may note that under these conditions Eqn. (45) becomes identical with Eqn. (27), which makes it possible to compare Eqn. (49) with Eqn. (29) and thus obtain

$$\text{HETS} = \frac{D_{\text{eff}}}{u} . \quad (50)$$

The resulting value of HETS differs significantly from the concept of HETP widely used at the present time in chromatography[22,23]:

$$\text{HETP} = \frac{2D_{\text{eff}}}{u_0} , \quad (51)$$

where u_0 is the velocity of the developer in a system of coordinates linked to the column. It is evidently of interest to compare these two concepts.

In the separation of a mixture on a stationary sorbent in a system of coordinates linked to the feed cross-section[11,21], there is a countercurrent of the eluent and the sorbent and the following equation applies:

$$u_0 = u + v . \quad (52)$$

Using Eqn. (27), it is possible to show that

$$u = u_0 \cdot \frac{k'}{1+k'} . \quad (53)$$

On substituting the value of u from Eqn. (53) in Eqn. (50), we obtain after some rearrangement the expression

$$\text{HETS} = \text{HETP} \cdot \frac{1+k'}{2k'} , \quad (54)$$

from which it follows that the values of HETS and HETP are identical only when $k' = 1$. When $k' \ll 1$, HETS differs significantly from HETP. We may note that, when $k' = 0$ (no sorption of the components to be separated), the concept of HETS loses significance, since this quantity tends to infinity, which is physically understandable because the absence of sorption of the components separated implies also the absence of chromatographic separation.

Eqns. (28) and (48) are used to determine HET in chromatography. Under conditions where $\tilde{\alpha} = \sqrt{\alpha}$, Eqn. (45) is transformed into Eqn. (17). On this basis (for any value of α), one can write

$$\text{HETS} = \frac{D_{\text{eff}_1}}{u} \cdot \frac{(\alpha+\sqrt{\alpha})\ln\alpha}{2(\alpha-1)} \cdot \frac{\frac{\sqrt{\alpha}-1}{\sqrt{\alpha}}}{\frac{\sqrt{\alpha}-1}{\sqrt{\alpha}}} = \frac{D_{\text{eff}_1}}{u} \cdot \frac{\frac{1}{2}\ln\alpha}{1-\frac{1}{\sqrt{\alpha}}} . \quad (55)$$

According to the literature data[17],

$$\text{HETS} = \text{HET} \cdot \frac{\ln\varepsilon}{1-\frac{1}{\varepsilon}} , \quad (56)$$

where

$$\varepsilon = k_2\lambda_0 = \sqrt{\alpha} . \quad (57)$$

Comparison of Eqns. (55) and (56) shows that

$$\mathrm{HET} = \frac{D_{\mathrm{eff}1}}{u} \quad . \tag{58}$$

3. The Validity of the Assumption that $D_1^* = D_2^*$

Eqn. (49) may be transformed into a formula analogous to the formulae for the calculation of the number of theoretical plates n in the chromatographic column[2,23,24]. Indeed, if it is assumed that $l = s_1^0$, then

$$2\ln q_0 = 2\ln\left[\frac{A_1 \cdot A_{\max 2}}{A_2 \cdot A_{\max 1}}\right] = 2\ln\left[\frac{A_{\max 2}}{A_2}\right] = \sigma^2_{\max} \quad , \tag{59}$$

where $\sigma_{\max_2}$ is the number of standard deviations at a specified peak height. According to Eqns. (49) and (54),

$$\sigma^2_{\max 2} = \frac{s_1^0}{\mathrm{HETP}} \cdot \frac{2k'}{1+k'}(\alpha - 1) \quad . \tag{60}$$

From Eqns. (47) and (53), we have

$$s_1^0 = \frac{u_0}{1+k'} \frac{k'}{1+k'} \cdot \frac{\alpha - 1}{2} \cdot t \quad . \tag{61}$$

On substituting Eqn. (61) in Eqn. (60), we obtain

$$t = \frac{\mathrm{HETP}}{u_0} \cdot \frac{\sigma^2_{\max 2}}{(\alpha-1)^2} \frac{(1+k')^2}{(k')^2} \quad . \tag{62}$$

Since

$$t = \frac{H}{u_0}(1+k') \quad , \tag{63}$$

where H is the height of the chromatographic column, it follows that

$$n = \frac{\sigma^2_{\max}}{(\alpha-1)^2}\left(\frac{1+k'}{k'}\right)^2 \quad . \tag{64}$$

According to Purnell[24],

$$n = \frac{36}{(\alpha-1)^2} \cdot \left(\frac{1+k'}{k'}\right)^2 \quad , \tag{65}$$

while according to Zhukhovitskii[23],

$$n = \frac{32K_1}{(\tilde{\alpha}-1)^2} = \frac{32K_1}{(\alpha-1)^2} \cdot \left(\frac{1+k'}{k'}\right)^2 \quad , \tag{66}$$

where K_1 is the separation criterion.

According to Martin[2],

$$n = \frac{16\sigma}{(\tilde{\alpha}-1)^2} = \frac{16\sigma}{(\alpha-1)^2} \cdot \left(\frac{1+k'}{k'}\right)^2 \quad . \tag{67}$$

Eqn. (64) is identical with Eqns. (65), (66), and (67). The conclusions based on the equations formulated (see, for example, Purnell and Quinn[24]) are satisfactorily confirmed in practical chromatographic analysis despite the assumption of the equality of D_1^* and D_2^*. Therefore Eqn. (49) derived here should also hold in practice both by analogy and as a result of its relation to the equations already available. Indeed, on the basis of Eqn. (49), one can imagine the way in which the transition from the periodic version of development-type circulation chromatography to its continuous separation version with periodic additional feed and take off may be achieved[5,11]. Without resorting to the above assumption, it is difficult to account for the real existence of continuous-operation chromatography such as the method proposed for gas chromatography by Pichler and Schulz[25].

4. Optimum Conditions for Chromatographic Separation

If the role of the chromatographic column consists only in the separation of the binary mixture to the required degree of purity (sufficient, for example, for analysis), then in principle it is possible to ensure conditions of chromatographic separation such that the work of separation is a minimum. The study of the optimum separation conditions in the general theory of separation leads to the conclusion that cascades with reduction of the fluxes from one separation element to another (and in the case of low separation factors cascades with a continuous variation of the fluxes) are most convenient. When certain laws governing the distribution of the fluxes and the relative concentrations (corresponding to the distribution in an ideal cascade) operate, the work of separation in such cascades is a minimum[10]. Bearing in mind the analogy found between a chromatographic column and an ideal cascade, it is therefore of interest to elucidate under what conditions the chromatographic column most closely approaches the ideal cascade.

According to Eqn. (45), when

$$\tilde{\alpha} = \sqrt{\alpha} \tag{68}$$

the volume ratio of the phase fluxes in the chromatographic column becomes equal to the analogous ratio in the ideal cascade [see Eqn. (17)]. Thus condition (68) may be called the optimum condition for chromatographic separation. From it and from the fundamental equation of the ideal cascade, it follows directly that under optimum conditions

$$\tilde{\alpha} = \beta \quad . \tag{69}$$

On substituting the values of $\tilde{\alpha}$ and β from Eqns. (15) and (46) in Eqn. (69) and using Eqn. (35), it is easy to show that condition (69) corresponds to the equality $u = v$. Consequently, judging from Eqns. (5) and (17), the equality

$$\frac{\varkappa_1}{\varkappa}\sqrt{k_2 k_1} = k'_{\mathrm{av}} = 1 \quad , \tag{70}$$

also constitutes a condition identical with the optimum condition.

It is remarkable that the limiting value of k', determined[24] from the condition for the minimum duration of analysis and corresponding to the complete absence of resistance to mass transfer in the stationery phase, is about 0.9, which is close to unity.

III. THE RELATIVE CONCENTRATION PARTITION LAW IN THE CHROMATOGRAPHIC CONCENTRATION OF ISOTOPES

Spedding et al.[1] succeeded for the first time in showing experimentally that, by observing the conditions[26] for the sharpening of the fronts of the chromatographic zone of a binary isotope mixture, it is possible to transfer the zone across a length of the sorbent bed exceeding by a factor of 50–100 the intrinsic length of the zone without the slightest spreading. An analogous result can evidently be arrived at with the aid of the thermal factor in chromatography[3,4]; the chromatographic enrichment method then becomes more economical[4], since the consumption of expensive chemical reagents is replaced by the consumption of low-potential heat.

Fig. 4 shows the stationary chromatographic zone of a binary isotope mixture moving down the bed of a stationary sorbent. In a system of coordinates linked to the zone, there exists[12,13] a countercurrent of the sorbent and the

solution and the flux of the mixture with the sorbent is equal to the flux of the mixture with the solution:

$$L' = \varkappa_1 v a_0 = \varkappa_2 c_0 \tag{71}$$

and

$$\frac{a_1}{a_2} = \text{const} \cdot \frac{c_1}{c_2} \ . \tag{72}$$

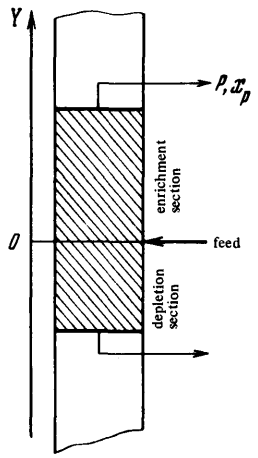

Figure 4. A stationary chromatographic zone.

The latter equation is valid when the sorbent is in thermodynamic equilibrium with the solution. Using Eqn. (71), one can also write[12,13]

$$\text{div}\, I = \frac{\partial x'}{\partial s} - \frac{\partial x''}{\partial s} - \frac{D_{\text{eff}}}{u} \frac{\partial^2 x'}{\partial s^2} \ . \tag{73}$$

At the instant of attainment of equilibrium div $I = 0$ and

$$\Delta x = x' - x'' = \frac{D_{\text{eff}}}{u} \cdot \frac{\partial x'}{\partial s} \ , \tag{74}$$

i.e. a concentration gradient is established in the zone such that the reverse diffusion flux will fully balance the entire flux of the first (extracted) component.

For substances with similar physicochemical characteristics ($\alpha - 1 \ll 1$), Eqn. (14) may be approximated[18] in the following way:

$$\Delta x = (\alpha - 1)\, x' (1 - x') \ . \tag{75}$$

On substituting Eqn. (75) in Eqn. (74), we obtain after integration

$$\xi_l = \xi_0 e^{lu/D_{\text{eff}}(\alpha - 1)} \ . \tag{76}$$

Hence, according to Eqn. (50)

$$N_{\min} = \frac{\ln q_0}{\alpha - 1} \ . \tag{77}$$

The resulting expression is the familiar Fenske equation[10] for the calculation of the number of theoretical separation stages in a rectangular cascade with total phase reversal. We may note that, for the chromatographic column under consideration, this equation could be formulated immediately, since Eqns. (71) and (72) in no way differ from the familiar equations[10] for mass transfer in a column with total phase reversal.

In the presence of take off[13] the expression for the flux of the first component through a cross-section in the enrichment section of the zone must be written in the following way:

$$I = L' \left[(\alpha - 1)\, x' (1 - x') - \frac{D_{\text{eff}}}{u} \frac{dx'}{ds} \right] + Px' \ , \tag{78}$$

where P is the take-off flux. At equilibrium a concentration gradient is established in the zone such that the reverse diffusion flux will balance the entire flux of the first component with the exception of the take-off flux:

$$\begin{gathered} L' \left[(\alpha - 1)\, x' (1 - x') - \frac{D_{\text{eff}}}{u} \cdot \frac{dx'}{ds} \right] + Px' = Px_p \ , \\ \frac{dx'}{ds} = \frac{u}{D_{\text{eff}}} (\alpha - 1)\, x' (1 - x') - \frac{u}{D_{\text{eff}}} \frac{P}{L'} (x_p - x') \ . \end{gathered} \tag{79}$$

Using Eqn. (50), it is easy to find that

$$\frac{dx'}{dN} = (\alpha - 1)\, x' (1 - x') - \frac{P}{L'} (x_p - x') \ , \tag{80}$$

i.e. the familiar mass-exchange equation[10] widely employed in the theory of isotope separation.

From the general theory of separation, it is known that[10] Eqn. (80) describes also the cascade in which the flux L' is a continuous function of the number of the stage with a maximum at the feed point. The overall flux is then

$$\Sigma L' = \int L'\, dN = \int L'\, dx' \frac{dN}{dx'} = \int \frac{dx'}{\frac{1}{L'} \cdot \frac{dx'}{dN}} \ . \tag{81}$$

In the ideal cascade the overall flux is a minimum[10,18,19]. According to Eqn. (81), the overall flux is a minimum when the integrand $x'(dN/dx')$ is a minimum for all x', i.e. when the reciprocal is a maximum:

$$\frac{1}{L'} \frac{dx'}{dN} = \frac{(\alpha - 1)\, x' (1 - x')}{L'} - \frac{P}{L'} \ . \tag{82}$$

From the condition for the maximum, i.e. by differentiating Eqn. (82) with respect to L' and putting $(\partial / \partial L')[(1/L')(\partial x'/\partial N)] = 0$, one can find[10]

$$L'_{\text{id}} = \frac{2P}{\alpha - 1} \cdot \frac{x_p - x'}{x' (1 - x')} \ . \tag{83}$$

On substituting Eqn. (83) in Eqn. (80) and integrating, we obtain Eqn. (29).

The expression for the flux at any stage in the cascade for any value of the separation factor has been obtained by the method of finite differences[27,28].

IV. NEW METHODS OF GAS CHROMATOGRAPHIC SEPARATION

Adsorption may be regarded[29] as a result of the attraction of gas molecules to adsorbent molecules. In consequence of this attraction, a potential force field is established above the adsorbent. If this field is regarded as constant at a certain distance h, then

$$a = ShC_0 e^{-\Delta v / kT} \ , \tag{84}$$

where Δv is the difference between the energy of the molecule near the adsorbent and in the gas phase and S is the surface area of the adsorbent.

We may note that an equation analogous to Eqn. (84) describes[29] also the distribution of molecules in the gravitational force field. In this connection a new method of gas-chromatographic separation of heavy element isotopes in the artificial gravitational field of a gas centrifuge (gas–gas chromatography) has been proposed recently[30]; it differs from the familiar method (in a countercurrent gas centrifuge[10]) to the same extent that gas–liquid chromatography differs from distillation.

The centrifuge[30] is a cylinder *1* rotating at a high angular velocity (Fig. 5). The internal wall of the cylinder is a porous partition *2* firmly bound to the cylinder. The partition has narrow channels, positioned at right angles to the axis of the apparatus, in which the molecules of the components separated can pass freely. Along the axis of the centrifuge, the carrier gas moves in a continuous stream. The channels in the partition are then also filled by the carrier gas and play a role analogous to that of adsorption centres in gas-adsorption chromatography. When the apparatus rotates, a gravitational field identical with the field of sorption forces is established.

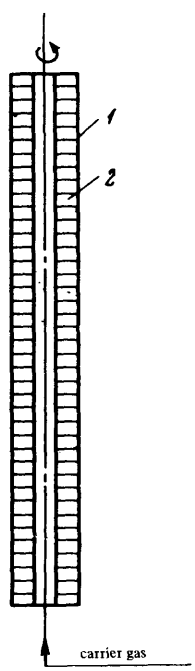

Figure 5. Gas centrifuge: *1*) cylinder; *2*) porous partition.

When a sample of the mixture to be separated is introduced into the stream of the carrier gas, zones corresponding to individual components may be obtained at the outlet from the apparatus by virtue of the repeated partitioning of the molecules of these components between the moving gas phase and the stationary phase and also by virtue of the difference in the partition of the components caused by the difference between their molecular weights Δm. In this case the separation factor is defined by the following equation[10]:

$$\alpha = e^{\Delta m\, \omega^2 \cdot \Delta r / kT}, \qquad (85)$$

where ω is the angular velocity of the gas centrifuge and r is the radius.

Large separation factors can be obtained only at relatively high angular velocities and correspondingly high rates of rotation (above 60 000 rev min^{-1}). Thus in the separation of uranium isotopes[10] in a countercurrent centrifuge with $\Delta r = 6$ cm for $\Delta m = 3$ g $mole^{-1}$, $k = 8.315 \times 10^7$ erg $mole^{-1}$ and $T = 300°K$, we would have $\alpha = 1.085$. Calculation[31] for a mixture of UF_6 containing uranium isotopes, carried out on the assumption that the difference in absorbability is determined by the difference between the zero-point energies, gives $(\Gamma_2 - \Gamma_1)/(\Gamma_2 + \Gamma_1) = 10^{-5}$.

To obtain small amounts of the isotopes of light and intermediate elements, thermal diffusion columns[10]—the simplest laboratory apparatus for isotope separation—are now widely employed. However, separation on thermal diffusion columns (as in the case of fractional distillation) requires comparatively large amounts of the initial mixture. In this connection the chromatographic method in a thermogravitational field is also of interest[21]. The separation factor in the thermal diffusion of a binary mixture is determined[10] by an equation of the following form:

$$\alpha = 1 + \delta \frac{\Delta T}{\bar{T}}, \qquad (86)$$

where

$$\delta = \frac{105}{108} \cdot \frac{\Delta m}{2m} \cdot R_T = \delta_0 R_T \qquad (87)$$

and R_T is a correction coefficient taking into account the nature of the intermolecular forces.

When the gravitational field of the gas centrifuge is brought into coincidence with the thermal field, it is evidently possible to achieve a method of gas-chromatographic separation which in many cases is not inferior to chromatography in a sorption field.

The analogy may be drawn further by considering other known methods of separation in countercurrent columns[10]. As usual, the choice of the method[10] will determine the value of the separation factor, the thermodynamic efficiency (characterising the energy consumption), the nature of the apparatus, and finally the conditions of the analysis or the scale of the process. In this connection it is useful to recall that the concept of the ideal cascade developed here leads to the introduction in chromatography of concepts such as the work of separation, the separating power, and the separating potential[10,18,19,32–34]. By calculating the cost of all things consumed in the operation of the separating column per hour, it is possible to calculate the cost per unit separating power when a particular technological procedure is employed. Clearly the best technological procedure is one which ensures the minimum cost per unit separating power. The calculation of the cost of one kilogram-separating unit per hour[32] is analogous to a comparison of separating apparatus in terms of the efficiency in real technological processes.

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Conjugation in the Series of Phosphorus(III) Compounds

E.N.Tsvetkov and M.I.Kabachnik

In its electronic effect phosphorus(III) is usually regarded as an analogue of tervalent nitrogen. However, in recent years it has been shown that substituents with phosphorus(III) do not exhibit a π-donor effect, which is characteristic to a greater or smaller extent of groups containing the elements in Periods II and III with lone pairs of electrons. On the other hand, substituents with phosphorus(III) exhibit a π-acceptor effect, characteristic of *meta*-orienting groups, and probably due to the interaction with the vacant orbitals of phosphorus. Thus, in contrast to elements of Periods II and III with lone electron pairs, phosphorus(III) is incapable of $p-\pi$ conjugation. The absence of the capacity of the lone electron pair of phosphorus to undergo delocalisation (or the presence of only insignificant capacity of this kind) has been explained by an enhanced *s*-character of the lone pair orbital, which is confirmed by data for the valence angles in phosphorus(III) compounds. The physical and chemical properties of phosphorus(III) compounds in which there is a possibility of $p-\pi$ conjugation are discussed in the review from this standpoint. All the properties are consistent with the hypothesis of the predominant *s*-character of the lone electron pair of phosphorus.
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I. INTRODUCTION

The development of the chemistry of organophosphorus compounds is to a considerable degree due to phosphorus(III) compounds, which, by virtue of their high reactivity, occupy an outstanding place among other types of organophosphorus derivatives. The most interesting reactions of phosphorus(III) compounds are accompanied by an increase in valence and the involvement of the lone pair in the formation of a new bond. Thus the properties of phosphorus(III) compounds associated with the participation of the lone pair in intermolecular electronic steps have been widely investigated. Nevertheless little is known about the nature of the lone electron pair of phosphorus and its intramolecular interactions with attached π-electronic systems. Phosphorus in the tervalent state is perhaps the only element in the Second and Third Period forming organic derivatives about the electronic effect of which there has been virtually no information until recently. By analogy with nitrogen and other elements with lone electron pairs and also according to its position in the Periodic System, it was usually postulated[1,2] that it should be an *ortho–para* directing substituent with a highly pronounced π-donor conjugation effect.

According to the classical concepts developed by the English School of Chemistry[3] the capacity of the lone electron pair of any atom for $p-\pi$ conjugation is associated with the position of the element in the Periodic System. Thus, within the limits of a single Period, it decreases from left to right and within the limits of a single Group from above downwards:

$$R_2N > RO > F;\ F > Cl > Br > I;\ RO > RS\ .$$

Later these qualitative relations were confirmed on the quantitative scale of resonance effects proposed by Taft[4,5].

Using these relations, one may expect that the effect of π-donor conjugation of substituents with phosphorus(III) will be greatest among the elements of the Third Period:

$$R_2P > RS > Cl$$

Compared with nitrogen, the effect should be only slightly reduced, to the same extent as on transition from oxygen to sulphur. Apart from π-donor conjugation, a π-acceptor d-orbital interaction effect, which is probably characteristic of all the elements in the Third Period but is shown in a pure form only in the case of silicon, can also be postulated for phosphorus(III). However, on the whole these comparisons might have led to the expectation that substituents with phosphorus(III) would be *ortho–para* directing and would exhibit a positive mesomeric effect.

However, the study of the chemical properties of phosphorus(III) compounds showed that, contrary to the above considerations, phosphorus is greatly inferior in its capacity for $p-\pi$ conjugation not only to nitrogen but even to sulphur and chlorine. Moreover, so far no property has been found involving a distinct effect of the capacity of the lone electron pair of phosphorus for $p-\pi$ conjugation in the ground state of the molecule. Therefore the above series should be reformulated as follows:

$$RS > Cl > R_2P\ .$$

Owing to the absence or insignificance of the π-donor effect, phosphorus(III) exhibits distinct π-acceptor properties, probably via $p_\pi - d_\pi$ conjugation and therefore belongs to *meta*-directing groups. Chemically this was demonstrated for the first time by the authors of the review together with Chang Jung-yu in experiments on the directive influence in the addition of secondary amines to vinyl derivatives of phosphorus(III).[6-8] Subsequently these conclusions were confirmed and developed by the present authors with other collaborators[9-15] and in a number of studies in the Soviet Union[16,17] and abroad[18-40].

In order to account for the unusual properties of phosphorus(III), we put forward a hypothesis together with Bochvar and Lobanov[9,11,12] according to which the reason for the lack of capacity for (or low tendency towards) $p-\pi$ conjugation of the lone electron pair of phosphorus(III) is due to the type of hybridisation of its orbital or more precisely its enhanced s character, which was confirmed by data on the geometry of phosphorus(III) compounds.

In the present review an attempt is made to examine consecutively from the standpoint of this hypothesis the physical and chemical properties of phosphorus(III) compounds in which an effect of $p-\pi$ conjugation is possible. In the first place much attention has been devoted to the structure of the electronic shell of phosphorus(III) and the geometry of its compounds. Next the physical and chemical properties associated with the lone electron pair of phosphorus in both ground and optically excited states are considered on the basis of these data.

We believe that such treatment is particularly necessary, since the view that phosphorus(III) is a complete analogue of nitrogen, which exhibits π-donor properties in aromatic and unsaturated compounds, has become firmly rooted in the literature. This view is sometimes encountered in monographs[1,2] without serious experimental justification. The problem of $p-\pi$ conjugation in phosphorus(III) compounds was partly dealt with in a recent monograph by Hudson[41] which has been translated into Russian. However, these problems are treated from traditional standpoints and the latest data which contradict the view expounded are not discussed.

II. THE STRUCTURE OF THE ELECTRONIC SHELL OF TRICOORDINATE PHOSPHORUS

A. GROUND STATE

The electronic shell of the neutral phosphorus atom contains 15 electrons. Ten of these are in the first and second quantum levels K and L ($1s^2 2s^2 2p^6$) and five occupy the s and p orbitals of the M valence shell ($3s^2 3p^3$). The latter has a further five unfilled d orbitals; the $3s$ and $3p$ orbitals do not differ in symmetry from the $2s$ and $2p$ orbitals but are more diffuse. The p orbitals are symmetrical relative to the three coordinate axes.

The symmetry of the d orbitals is more complex. Their distribution in space is shown in Fig. 1, where each of the five d orbitals is presented separately, and also in Fig. 2, where a steric model of superimposed d orbitals is shown. In the isolated atom all the d orbitals are energetically equivalent (degenerate). Under the influence of the electric fields of adjacent atoms, the energy levels of the d orbitals are split into two groups: d_γ orbitals (d_{z^2} and $d_{x^2-y^2}$) directed along the coordinate axes and having lower energies, and d_ϵ orbitals (d_{xy}, d_{xz}, and d_{yz}), which have maxima at 45° to the coordinate axes. Apart from the s and p orbitals, the d_γ orbitals (sp^3d and sp^3d^2 hybridisations) are usually employed in the formation of σ bonds. The d_ϵ orbitals probably participate in the formation of $p_\pi - d_\pi$ bonds.

The energy difference between the $3s$ and $3p$ orbitals of phosphorus is less than between the $2s$ and $2p$ orbitals of

nitrogen[41] (Fig. 3). The valence shell of the latter also consists of five electrons ($2s^2 2p^3$), but, in contrast to phosphorus, it does not have d orbitals in the same quantum level. Therefore the transition of the valence electrons of nitrogen to the d orbital (for example $2s \rightarrow 3d$) is coupled with a greater energy expenditure (about 530 kcal mole^{-1}) than the analogous transition of phosphorus electrons ($3s \rightarrow 3d$, 380 kcal mole^{-1}). It appears that in many ways this difference is responsible for the specific features of phosphorus chemistry. Possibly other higher phosphorus levels (4s, 4p) also have an effect. The energy levels of the electronic configurations of the unionised phosphorus atom (based on spectroscopic data) are quoted in van Wazer's book[42].

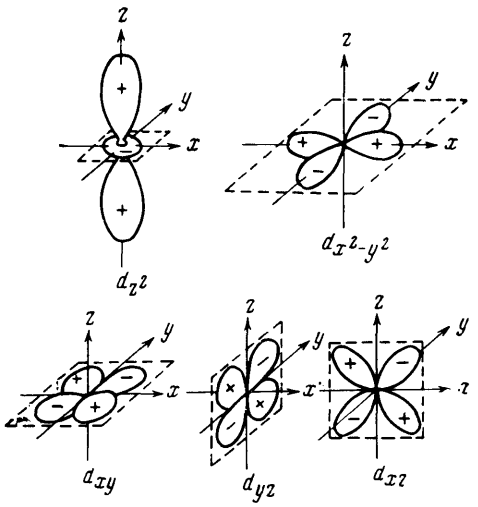


Figure 1. The form and relative orientations in space of d orbitals[359].

B. VALENCE STATE

The valence state of phosphorus(III), i.e. the state of the electrons of its valence shell on formation of three σ bonds, naturally differs from the ground state. According to the quantum-mechanical theory of valence[43,45] in its simplest form, when bonds are formed by any atom, for example phosphorus, nitrogen, oxygen, or sulphur, p orbitals are employed, since they give rise to stronger bonds than s orbitals (the strength is 1 for the 2s orbital and 1.732 for the 2p orbital). Accordingly, the angles in the compounds of the above elements, for example in hydrides, should be 90°. Indeed, in the case of the hydrides of phosphorus, sulphur, and higher analogues the valence angles only slightly exceed 90° (Table 1). However, ammonia and water have almost tetrahedral valence angles. The increase of the valence angle, even if only slight, is evidence of a deviation of the valence state from the ground state.

The orientation of bonds in a particular direction in space is explained in valence theory by the directed orientation of p and d orbitals. Geometry inconsistent with their configurations is regarded as a result of hybridisation with other orbitals, in particular s orbitals. The hybrid $s-p$ orbitals form stronger bonds than the pure p orbital (the strength for the sp^3 orbital is 2) and therefore the tetrahedral configuration is the most favourable from this point of view. However, the tendency for molecules with lone pairs of electrons to form a tetrahedral configuration is counteracted by the opposing tendency to retain the lone s electron pair, since the latter has the lowest energy. As a result, the valence angle assumes an intermediate value between the right angle and the tetrahedral angle. The above considerations do not of course explain the differences in the geometries of the molecules in the Second and Third Periods. The reasons for these differences in valence angles are much more complex.

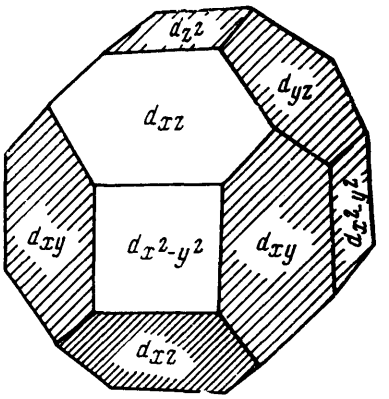


Figure 2. A steric model of superimposed d orbitals[360].

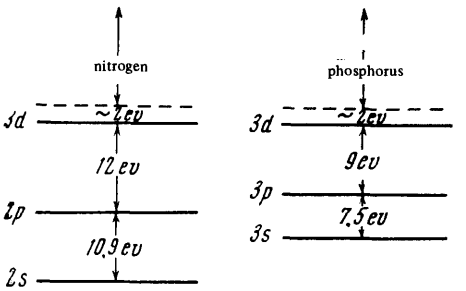


Figure 3. Atomic energy levels of nitrogen and phosphorus[41].

At the present time there exist two approaches to this problem, according to one of which, based on valence theory, the main reason for the increase of valence angles is the Coulombic repulsion of the atoms linked to the central element. This hypothesis was put forward for the first time by Pauling[43,44]. Subsequently the Coulombic and exchange repulsion of bonding electrons was also taken into account.[45] These factors should play a smaller role in the case of central atoms with large radii and therefore the repulsion and correspondingly the valence angles should be greater for compounds of elements of the Second

Period. Mulliken[54] calculated the repulsion energy of hydrogen atoms in the phosphine molecule and showed that, owing to the large radius of the phosphorus atom, it is smaller by a factor of approximately 3 than for ammonia (the N–H and P–H bond lengths are respectively 1.014 and 1.414 Å). Even when the valence angle in PH_3 is altered to 90° and in NH_3 to 120°, the repulsion energy in the first case is smaller by a factor of approximately 2 than in the second. In his examination of these problems from the standpoint of valence theory and the LCAO-MO method, Mulliken concluded that, apart from the repulsion of atoms not linked by valence bonds, account must be taken also of $p-d$ hybridisation, which gives rise to additional stabilisation of the pyramidal phosphine molecule compared with ammonia. Analogous reasoning is applied also to Group VI elements.

Table 1.

Molecule	Valence angle, deg	References	Molecule	Valence angle, deg	References
NH_3	107.3	46	H_2O	104.5	50
PH_3	93.8	47	H_2S	92.1	51
AsH_3	91.8	48	H_2Se	91.0	52
SbH_3	91.3	49	H_2Tl	89.5	53

Recently Hutchinson[55] examined this problem from the standpoint of the strength of hybrid bonds or more precisely the values of the overlap integrals for the s and p orbitals. It was found that the increase of the amount of s character in the hybrid orbitals of elements of the Second Period and the correspondingly greater deviation from a valence angle of 90° leads to an increase of bond strength, since the overlap integral for 2s orbitals is greater than for 2p orbitals. This is not observed in the Third Period and therefore the deviations from an angle of 90° are in this case minimal.

Thus both valence theory and the LCAO-MO method yield merely a qualitative treatment and do not provide an answer to the question why the valence angles in compounds of the elements of the Second Period are close to the tetrahedral value, while in the remaining compounds they are approximately 90°. This was probably the reason for the development of an alternative theory of directed valences—the theory of the repulsion of electron pairs in the valence shell (see for example Refs. 56 and 57 and the literature quoted therein). According to this theory, the formation of directed bonds is due to the repulsion, in consequence of the operation of the Pauli principle, of the electron pairs of the valence shell and the latter can be both unshared and involved in bond formation. In the case of four equivalent pairs, their repulsion leads to the formation of a tetrahedral configuration. The repulsion between lone pairs is more pronounced (the pair occupies a larger proportion of the valence shell) than between bonding pairs, since the latter are located in the field of two nuclei. Accordingly the valence angles of molecules with lone electron pairs are somewhat smaller than the tetrahedral value and this increases on passing from one to two lone pairs (ammonia and water; see Table 1).

In contrast to the elements of the Second Period, the valence shells of which have only four electron pairs, the elements of the Third Period are capable of expanding the valence shell to six electron pairs. Theoretically the number of electron pairs can reach nine but compounds with such coordination have not so far been found. The most likely distribution of these electron pairs is along the angles of a regular octahedron. The bonds formed by these pairs will be at right angles to one another. Probably the 90° angle is limiting and its further decrease involves considerable repulsive forces. The decrease of the limiting valence angle from 109°28′ to 90° on passing from elements in the Second Period to those in higher Periods can be accounted for by the increase of the radius and the decrease of the electronegativity of the central atom, which leads to the removal of the lone pairs to a greater distance from the nucleus and a decrease of the repulsion between them. Thus the repulsion between the lone and shared pairs in elements of the Third and higher Periods leads to a greater mutual approach of the bonds, up to the limiting angle of 90°.

With the aid of this purely qualitative concept and certain auxiliary postulates, it is possible to account for the geometry of a large number of compounds. We may note that recently Bader and Preston[58] criticised these hypotheses.

Whatever the reasons for the differences between the valence angles in elements of the Second Period and higher Periods, the fact of this difference is itself important, since it indicates a difference between the valence states of the elements in these Periods within the limits of a single subgroup, or, in other words, a difference in the nature of the hybridisation of their atomic orbitals.

In order to determine the type of hybridisation, it is possible to employ data for the geometry of molecules and also certain physical methods (nuclear magnetic resonance and nuclear quadrupole resonance).

According to the theory of directed valences, valence angles are determined by the nature of the hybridisation of atomic orbitals. Thus, knowing the valence angles, it is possible to determine the type of hybridisation of the relevant atom in different compounds. However, the use of this principle requires certain assumptions. In the first place it is necessary to assume that the interorbital and internuclear angles are the same, i.e. the bonds are not "bent". For elements the valence shells of which contain only s and p electrons, for example nitrogen, this assumption is quite sufficient to determine the nature of hybridisation, since there is an unambiguous relation between the interorbital angle and the type of $s-p$ hybridisation. The problem of the valence state of elements in higher Periods, in particular phosphorus, is much more complex. The third quantum level contains, apart from the s and p orbitals, also d orbitals, which may be involved in hybridisation. Therefore, in the presence of several types of branching, it is necessary to select orbitals responsible for hybridisation, which always involves certain assumptions. Otherwise several different valence states will correspond to a single valence angle. For example, in phosphorus, which has three types of orbitals, the valence angle of 90° may be due to both the p_3 state and sp^3-d^2 hybridisation.

In determining the type of hybridisation of phosphorus(III) orbitals, one usually starts with the hypothesis that σ bonds are formed by s-p hybrid orbitals. The role of d orbitals in the formation of phosphorus(III) σ bonds is regarded as insignificant and is neglected. However, d orbitals can participate in the formation of π bonds (partial

double bond character). This hybridisation scheme was adopted in a number of studies for the theoretical interpretation of the NMR chemical shifts[59-62], in a discussion of dipole moments and quadrupole interaction constants for halides of Group V elements[63], in quantum-chemical calculations for phosphorus(III) and phosphorus(V) compounds[64-66], and in a number of other investigations[42].

However, we must point out that certain authors considered it necessary to invoke *d* orbitals in order to account for the geometry of the hydrides of Group V elements. Thus in calculations on phosphine Boyd and Lipscomb[67] thought it necessary to take into account the *d* orbitals, since best agreement with experimental data is then obtained. Mulliken used *d* orbitals in a discussion of the valence angles in phosphine[54]. Gordy and coworkers[48-50] considered the valence angles in the hydrides of arsenic, antimony, and sulphur and pointed out the inconsistency between the types of hybridisation determined from the valence angles and from the quadrupole interaction constants; they believe that the reason for this is the absence of an unambiguous correlation between the valence angles and the degree of *sp* hybridisation for elements where *d* orbitals can participate in hybridisation. We may note that the lack of agreement between the results obtained with the aid of the two different approximate methods cannot alone be regarded as proof of the participation of *d* orbitals in hybridisation, but it does demonstrate yet again the approximate nature of the method used to determine the type of hybridisation from the valence angles.

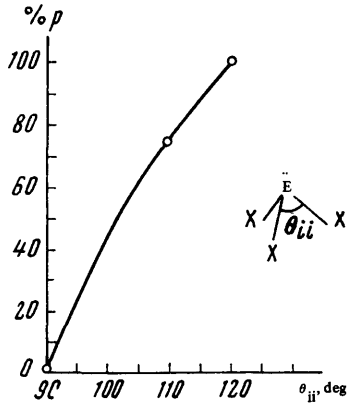


Figure 4. Variation of the percentage *p* character of the orbital of the lone electron pair with the valence angle θ_{ii} for symmetrical EX_3 molecules.

In order to assess the type of hybridisation of the orbitals of the lone electron pair of phosphorus or another element in the molecule of the type EX_3, one may employ a plot relating the amount of *p* character of this orbital to the X–E–X valence angle θ_{ii} (Fig. 4). We constructed such a plot[11] on the basis of three reference points corresponding to the *s*, sp^3, and *p* states of the lone pair. In the *s* state the X–E–X angle formed by the pure *p* orbitals is 90°. When the angle θ_{ii} increases, the amount of *p* character of the lone electron pair will increase and will reach 75% for the tetrahedral configuration (sp^3 hybridisation, 109°28 angle). Therefore an X–E–X angle of 120° (sp^2 hybridisation) will correspond to the full *p* character of the lone electron pair. An analytical expression for this relation was found[12] from the condition for the orthogonality of the hybrid atomic orbitals:

$$\% p = \frac{3\cos\theta_{ii}}{\cos\theta_{ii} - 1} \cdot 100\ \% . \qquad (1)$$

As already stated above, the valence angle in phosphine is approximately 94°C. When methyl groups are combined with the phosphorus atom, the valence angles increase and reach 99° for trimethylphosphine (Table 2).

Table 2. Valence angles in compounds of the type R_nPH_{3-n} ($n = 0-3$).

Compound	Angles			References
	H–P–H	H–P–C	C–P–C	
PH_3	93.8°	—	—	47
CH_3PH_2	93°23′	97°30′	—	68
$(CH_3)_2PH$	—	96°57′	99°43′	69
$(CH_3)_3P$	—	—	99.1°	70
$(C_6H_5)_3P$	—	—	103.0°*	71
$(C_6H_5)_2PC_6H_4Br$-*p*	—	—	103°*	72
$(C_6H_5C\equiv C)_3P$	—	—	100.7°*	73

*The average valence angle is quoted for the crystal.

In general a valence angle of about 100° is characteristic of the majority of phosphorus(III) compounds and the angle does not usually depend significantly on the type of substituents†. Compounds with methyl, aryl, alkoxy-, dialkylamino-,[77] or halogeno-groups have this angle (Table 3). The valence angles of cyclic compounds (cyclopolyphosphines, phosphorous anhydride) are also close to 100° or somewhat lower[86].

Table 3. Valence angles in compounds of the type PX_3.

X	X-P-X angle, deg	References	X	X-P-X angle, deg	References
F	100.104	78,79	CN	93.5	83
Cl	100	80	C_2H_5O	96.5	84
Br	101.5	81	H_3Si	96.45	85
I	102	82			

Gillespie[56] explained the slight increase of valence angles in phosphorus trihalides on passing from chlorine to iodine (Table 3) by the decrease of electronegativity and the increase of the atomic radius of the halogen. The anomalous (from the standpoint of this relation) angle in phosphorus trifluoride (104°) was regarded as due to a certain amount of double bond character of the P–F bonds, which arises owing to the partial transfer of the lone pair of fluorine to the vacant orbitals of phosphorus or, in

† The 120° valence angle, postulated in trisilylphosphine on the basis of spectroscopic data[74], was not confirmed by an electron diffraction study (Table 3). The valence angle of the phosphorus atom in tri-(*o*-tolyl)-phosphine (117°), calculated by Schindebauer from the dipole moment of this compound[75], is probably incorrect[76].

other words, owing to $p_\pi - d_\pi$ bonding. The increase of electron density in the bonds leads to an increase of the repulsion forces and an increase of the valence angles. Since the mesomeric effect is more pronounced for fluorine than for chlorine, the valence angles in phosphorus trifluoride are greater than in phosphorus trichloride. The hypothesis of $p_\pi - d_\pi$ bonding can probably be used to account for the valence angle of about 100° in the majority of phosphorus(III) compounds, since all the substituents enumerated above, which give rise to this type of angle, are capable of $p_\pi - d_\pi$ interaction (for the methyl group, hyperconjugation is possible). From this point of view, it is interesting that the valence angles in the nitrile group, which is incapable of such conjugation, do not differ from those in phosphine. This applies also to the silyl group, despite its considerable bulk‡.

If this hypothesis is correct, Eqn. (1) will yield a high value for the amount of p character of the lone electron pair, since it was derived on the assumption that the valence angles deviate from 90° only due to s-p hybridisation and no account is taken of the possible additional $p_\pi - d_\pi$ bonding factor and its effect on the geometry of the molecule.

Table 4. The nature of the hybridisation of the lone electron pair of phosphorus in phosphines according to ^{1}H NMR data.

Compound	J_{P-H}, Hz	References	s_p, %	p-character of lone electron pair, %
PH_3	182.2 *	89	6.2	19
CH_3PH_2	+ 187.83 ± 0.03	88	6.4	26
$(CH_3)_2PH$	+ 191.03 ± 0.03	88	6.5	34
$(CH_3)_3P$	—		13.7	41
$C_6H_5PH_2$	201 ± 4 *	90	6.8	32
$(C_6H_5)_2PH$	239 ± 4 *	90	8.2	45
$(C_6H_5)_3P$	—		18.4	55

*J_{P-H} was assumed to be the same as in methylphosphines.

The use of Eqn. (1) leads to the conclusion that, for the majority of phosphorus(III) compounds, the amount of p character of the lone electron pair is 40–50%, which corresponds to an angle of 100° ± 1°. In unsubstituted phosphine, primary phosphines, and trisilyl- and tricyanophosphines, the lone electron pairs have predominantly s character.

For primary and secondary phosphines, the spin–spin splitting constants J_{P-H}, which depend on the amount of s character (s_p, %) of the phosphorus orbital in the P–H bond, can also be used to estimate the nature of the hybridisation of the lone electron pair [88]:

$$J_{P-H} = 29.30\, s_p \qquad (2)$$

This method, based on the same assumptions as the one described above, permits an approximate assessment of the nature of hybridisation in those cases where there are no data for the geometry of the molecule. If it is assumed that the amount of s character of the phosphorus orbital in the P–C bonds of primary and secondary phosphines is the same as in tertiary phosphines (i.e. is clearly too high), then it is possible to calculate by Eqns. (1) and (2) the percentage of s character in the bonding phosphorus orbitals and in the orbital of the lone electron pair. Table 4 lists the values of J_{P-H} for primary and secondary phosphines, the contribution of s_p hybridisation, and the percentage of p character of the lone electron pairs in these compounds; however, these data must of course be regarded as only approximate.

It has been stated that in many cases the ^{31}P NMR chemical shifts for phosphorus(III) compounds can be used for the same purposes [60].

The valence angles in nitrogen(III) compounds are usually larger than in the corresponding phosphines and in ammonia and alkylamines are close to the tetrahedral value (Table 5). The introduction at the nitrogen atom of substituents capable of $p-\pi$ conjugation [phenyl and carbonyl groups and a phosphorus(III) or phosphoryl group [77]] increases the valence angles approximately by 10° to a value approaching 120°. Correspondingly, the lone electron pair of nitrogen is of the p type to the extent of 70% and above. In those cases where the valence angle is close to 120° the lone electron pair is almost entirely of the p type.

Thus the assessment of the type of hybridisation from valence angles or by other methods leads to the conclusion that the lone electron pair of phosphorus(III) differs from that in nitrogen in analogous compounds by having a much smaller amount of p character. An increase of the amount of p character is also observed on passing from phosphorus to sulphur.

Table 5. Valence angles in compounds of the type R_nNH_{3-n} (n = 0–3).

Compound	Angles			References
	H–N–H, deg	H–N–C, deg	C–N–C, deg	
NH_3	107.3	—	—	46
CH_3NH_2	105.8	112.2	—	91
$(CH_3)_2NH$	—	108.8	112.2	92
$(CH_3)_3N$	—	—	110.6	93
$(C_6H_5)_3N$	—	—	116	94
$HCONH_2$	118.53	120.37	—	95
$C_6H_5N(CH_3)_2$	—	—	116 *	96
$(SiH_3)_3N$	—	—	119.6 **	97
$(CH_3)_2NPCl_2$	—	—	120 *	77
$(CH_3)_2NP(O)Cl_2$	—	—	116 *	77

*Average angle at the N atom.
**Si–N–Si angle.

In contrast to phosphorus, sulphur has a second lone electron pair. With a valence angle of 90°, σ bonds should be formed by pure p orbitals. Then, if one of the lone pairs is fully of the s type, the other is a purely p electron pair. In the hybridisation of the orbitals of the lone electron pairs the amount of p character will vary from 100 to 50% (sp hybridisation). When the hydrogen atoms in hydrogen sulphide are replaced by alkyl or aryl

‡ We may note that the valence angles of the tricyanomethane anion [87], an electronic analogue of tricyanophosphine, amount to about 119.5° in $NH_4C(CN)_3$.

groups, the valence angles are found to increase (Table 6) with a corresponding increase of the amount of p character of the lone electron pairs, which reaches about 72% in the case of diphenyl sulphide§.

Chlorine has three lone electron pairs of which one may be of the s type and the other two of the p type in the limiting case. For sp^2 hybridisation, the amount of p character of any of the lone electron pairs will be 66.6%.

Table 6. Angles in compounds of the type R_nSH_{2-n} ($n = 0-2$).

Compound	Angles			References
	H—S—H, deg	H—S—C, deg	C—S—C, deg	
H_2S	92.1	—	—	51
CH_3SH	—	96°30′	—	98
$(CH_3)_2S$	—	—	98°54′	99
$(C_6H_5)_2S$	—	—	113°	100,101
		—		

Thus a distinctive feature of the structure of the valence shell of phosphorus(III) is a reduced amount of p character of the lone electron pair compared with the other elements of Periods II and III. This feature is reflected in the physical and chemical properties and in the capacity of the lone electron pair for $p-\pi$ conjugation.

III. $p-\pi$ CONJUGATION AND THE HYBRIDISATION OF THE LONE PAIR OF ELECTRONS

As already stated in the introduction, the capacity of the lone electron pair of any element for $p-\pi$ conjugation depends on the position of this element in the Periodic System and hence on the quantum level where the lone pair is located and, within the limits of a single Period, on the nuclear charge or the electronegativity of the element.

Yet another factor, which is usually hardly taken into account, namely the nature of the hybridisation of the electron pair¶, should play an important role[12]. Indeed, p or d orbitals are necessary for the formation of π bonds; s orbitals are incapable of interaction with p_Z orbitals, since the overlap integral S_{AB} of the s orbital of the A atom with the p_Z orbital of the B atom is zero[45], as shown in Fig. 5 taken from Coulson's book[45]. It follows from Fig. 5 that, by virtue of the difference in sign between the two parts of the p function, the integrand in $S_{AB} = \int \Psi_A \Psi_B \, d\tau$ is the sum of two terms equal in magnitude but opposite in sign (the elements $d\tau_1$ and $d\tau_2$ located symmetrically relative to AB axis correspond to these terms)[45]. The overlap integral becomes zero by virtue of symmetry properties. Thus p and sp hybrid lone electron pairs are capable of $p-\pi$ conjugation and in the latter case the capacity for conjugation is determined by the amount of p character of the lone pair.

§ The amount of p character of the orbital forming the σ bond was calculated from the formula

$$p = \frac{1}{1-\cos\theta_{ii}} \cdot 100\,\%,$$

where θ_{ii} is the valence angle.

¶ This problem was dealt with very briefly by Higashi et al.[102]

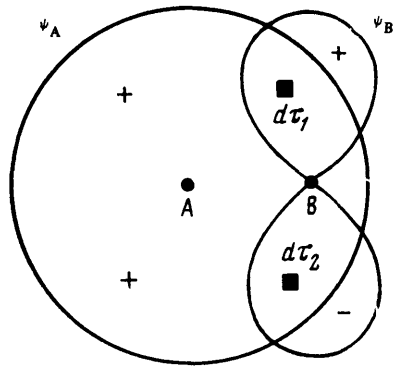


Figure 5. Schematic illustration[45] of the equality to zero of the S_{AB} overlap integral of the s orbital (Ψ_A) with the p_Z orbital (Ψ_B).

As shown above, the lone electron pair of phosphorus has a reduced amount of p character compared with the lone pairs of nitrogen, sulphur, and other elements in Periods II and III. Thus one may expect that in the case of phosphorus(III) $p-\pi$ conjugation in the ground state will be either greatly weakened and masked by other effects or, when the percentage of p character is very small, will be absent altogether. The experimental confirmation of this conclusion will be discussed below.

IV. PROPERTIES OF PHOSPHORUS(III) COMPOUNDS IN THE OPTICALLY UNEXCITED STATE

A. PHYSICAL PROPERTIES

1. Configuration Stability of Phosphorus(III) Compounds

A remarkable property of phosphorus(III) compounds is their configurational stability, which leads to optical activity in asymmetric molecules. This characteristic, which very sharply distinguishes phosphorus(III) compounds from the corresponding nitrogen(III) derivatives, is caused by the high energy barrier to the inversion of the pyramidal configuration of phosphorus associated with the high deformation energy of its valence angles. Theoretical calculations of the energy barrier to inversion yielded different results†. Here we shall note only the most correct calculations by Weston[108], which indicate that optically active phosphines may exist. Weston showed that phosphines have much higher energy barriers to inversion than amines (Table 7) and calculated the rate constants for their racemisation. For trimethylphosphine, the period of 50% racemisation at 20°C proved to be about 1 h. Hence Weston concluded that the optical isomerism of phosphines can be observed only at low temperature. Horner and Winkler[107] showed experimentally that optically active phosphines are more stable (in the sense of the retention of their configuration) than follows from Weston's calculations. They not only retain their optical activity at room temperature but can also be distilled without appreciable racemisation. Measurements of the rate of racemisation

† A good description of the history of this problem is given in McEwen's review[103]; see also other reviews[104,105].

at 130°C gave a high activation energy for the racemisation of dextrorotatory methylphenylpropylphosphine (about 30 kcal mole^{-1}). For the less stable diphosphines[108], where a rapid change in configuration occurs above 125°C, the activation energy for inversion is 26 ± 2 kcal mole^{-1} according to NMR data. It is interesting that changes in configuration are also not observed in many reactions involving the lone electron pair[103]. Configurational stability is characteristic not only of phosphines but also of the esters of phosphorus(III) acids, as shown by the geometrical isomerism of a number of five- and six-membered cyclic phosphites observed by the NMR method[109-119].

Table 7. Barriers to inversion of compounds of Group V elements according to spectroscopic data[106].

Compound	Inversion barrier, kcal mole^{-1}	Compound	Inversion barrier, kcal mole^{-1}	Compound	Inversion barrier, kcal mole^{-1}
NH_3	5.93	$P(CH_3)_3$	22.0	AsH_3	35.0
$N(CH_3)_3$	8.19	PF_3	45.1	$As(CH_3)_3$	29.2
PH_3	31.8	PCl_3	68.1	$Sb(CH_3)_3$	26.7

Thus phosphorus differs from nitrogen not only by the smaller valence angles but also by the stability of the pyramidal configuration, the change in valence angles requiring a significant expenditure of energy. The stability of the configuration has a most direct bearing on the problem of $p-\pi$ conjugation. The point is that, for $p-\pi$ conjugation to be appreciable, a significant increase of the amount of p character of the lone pair and a corresponding increase in valence angles is necessary. Then the energy expenditure on the deformation of valence angles cannot be compensated by the conjugation energy, since even in the most favourable case (conjugation of the amino-group with the benzene ring) the resonance energy does not exceed[117] about 10 kcal mole^{-1} and for the phosphino-group it can be considerably less. Hence it becomes understandable why valence angles at the phosphorus atoms do not increase even in the presence of substituents capable of conjugation with the lone electron pair.

Probably the above relation between the optical activity of phosphines and the low tendency of the lone electron pair of phosphorus towards $p-\pi$ conjugation is more general and is not characteristic solely of phosphorus. One may suppose that the absence of $p-\pi$ conjugation (or only insignificant conjugation) can be expected for those classes of compounds, asymmetric representatives of which can exist in an optically active form despite the presence of lone electron pair at the asymmetric central atom. This criterion may be employed in the discussion of the problems of $p-\pi$ conjugation in those cases where the molecular geometry is unknown.

2. Dipole Moments of Phosphines

In a discussion of the dipole moments of phosphines in connection with the problems of $p-\pi$ conjugation, three problems are of primary interest: the effect on the dipole moments of the nature of hybridisation of the phosphorus orbitals; the direction of the dipole moment in aliphatic and aromatic phosphines; the magnitude and direction of the mesomeric dipole moment.

Table 8 lists the dipole moments of unsubstituted phosphine, primary, secondary, and tertiary phosphines, and also ammonia and the corresponding amines. The lower dipole moment of unsubstituted phosphine compared with ammonia shows in particular that, in contrast to the lone pair of nitrogen, that of phosphorus makes an insignificant contribution to the overall dipole moment of the molecule. This is probably evidence of a greater amount of s character of the lone electron pair of phosphorus compared with nitrogen[125]. When the hydrogen atoms in phosphine are replaced by alkyl groups, a gradual increase of the dipole moment is observed, which is probably due, on the one hand, to the positive inductive effect of the alkyl groups and, on the other hand, to the increase of the moment of the lone pair due to the increase in the amount of its p character. It is interesting to note that the opposite tendency obtains for amines; on passing from ammonia to tertiary amines, the dipole moment falls (Table 8). Possibly this is caused by a lowering of the moment of the lone electron pair[125] as a result of the increase in the amount of its p character. The point is that the purely s and p electron pairs do not have a dipole moment by virtue of the symmetry of their orbitals[102]. Hybridisation leads to the appearance of a dipole moment, which is a maximum in the case of the sp state. An increase in the amount of p character of the lone electron pair from 50 to 100% or its decrease from 50 to 0% will reduce the dipole moment. These opposed tendencies in the variation of the dipole moments of amines and phosphines yet again demonstrate the different natures of their lone electron pairs.

Table 8. Dipole moments of aliphatic phosphines and amines.

Type of compound	Dipole moment			
	X=P	References	X = N	References
XH_3	0.579±0.012, gas	118	1.47, gas	119
CH_3XH_2	1.100±0.010, gas	68	1.283, gas	120
$C_2H_5XH_2$	1.17 ±0.02, gas	121	1.225, gas	122
	1.11 ±0.05, benzene	121		
$(CH_3)_2XH$	1.23 ±0.01, gas	69	1.02, gas	123
$(C_2H_5)_2XH$	1.39 ±0.06, benzene	121	0.920, gas	122
$(CH_3)_3X$	1.192±0.005, gas	70	0.612±0.003, gas	93,124
$(C_2H_5)_3X$	1.45 ±0.05, benzene	121	0.660, gas	122

The direction of the dipole moments in aromatic phosphines was determined by Sutton and coworkers[126], Klages and Langpape[127]‡, and also Schindlbauer and Hajek[129]. The direction of the moments in aliphatic amines and phosphines is the same, the negative pole of the dipole being located at the heteroatom. In aromatic amines the sign of the dipole moment changes as a result of $p-\pi$ conjugation and the benzene ring becomes the negative pole. On the other hand, in aromatic phosphines the direction of the dipole moment is maintained: the negative pole is the phosphorus atom as before. This follows from a comparison of the dipole moments of *para*-substituted phosphines: electron-donating substituents in the *para*-position increase and electronegative substituents decrease the moment (Table 9). A similar phenomenon is observed

‡ Klages and Langpape[127] quote unduly high dipole moments of trialkylphosphines, which were not confirmed by subsequent studies[121,128].

also in halogenobenzenes. Here too the direction of the dipole moment also remains unchanged, but its magnitude is reduced, mainly owing to $p-\pi$ conjugation[1]. In this case the mesomeric moment can be readily estimated approximately by Sutton's rule[1,130,131], namely from the difference between the dipole moments of aromatic and aliphatic compounds. This rule is known to apply only to regular groups, the direction of the dipole moments of which coincides with the direction of the benzene ring–substituent bond. In other cases vector subtraction is necessary. The mesomeric moment of dialkylphosphino-groups has not yet been determined. However, simple comparison of the dipole moments of aromatic and aliphatic compounds can lead to certain interesting conclusions. Thus, on passing from trimethylphosphine to dimethylphenylphosphine, a slight increase of the dipole moment is observed (Table 10). When a correction is applied for the effect of the solvent[121], the difference is somewhat reduced.

Table 9. Effect of *para*-substitution on the dipole moments of aromatic phosphines and amines.

Type of compound	Dipole moments			
	X = P	References	X = N	References
$C_6H_5XH_2$	1.11, hexane	129	1.54, hexane	129
p-$CH_3C_6H_4XH_2$	1.41, hexane	129	1.35, hexane	129
$C_6H_5X(C_4H_9)_2$	1.45, hexane	129	1.91, hexane	129
p-$CH_3C_6H_4X(C_4H_9)_2$	1.55, hexane	129	1.57, hexane	129
$(C_6H_5)_3X$	1.49, benzene	128		
$(p$-$CH_3C_6H_4)_3X$	1.92, cyclohexane	127		
$(p$-$Cl(C_6H_4)_3X$	0.65, benzene	126		

The decrease of the dipole moment may be due to the inductive effect of the phenyl group and the effect of $p-\pi$ conjugation (when it occurs). The moment may increase owing to $p_\pi-d_\pi$ conjugation or as a result of an increase in the moment of the lone electron pair (an increase in the valence angle). One may assume that the valence angles do not change significantly when the methyl group is replaced by a phenyl group. Since there is no decrease of the dipole moment on passing from trimethylphosphine to dimethylphenylphosphine, one must conclude that $p-\pi$ conjugation does not play an appreciable role and the mesomeric effect is due to $p_\pi-d_\pi$ conjugation. This conclusion is confirmed by a comparison of the moments of other aliphatic and aromatic phosphines (Table 9)§.

The weak π-donor capacity of phosphorus is indicated also by the dipole moments of phosphinoboranes R_2BPR_2 determined by Coates and Livingstone[132]. The lone electron pair of phosphorus interacts to a very slight degree (if at all) with the vacant p orbital of boron. Here phosphorus also constitutes the negative pole of the dipole. As a result of the conjugation of the lone electron pair of nitrogen with the p orbital of boron, in dialkylamino-boranes the negative pole is displaced to boron. Coates and Livingstone find this behaviour of phosphorus surprising and account for it by the different dimensions of the $2p$ orbital of boron and the $3p$ orbital of phosphorus. Without denying the role of this factor, we may, however, point out that the principal cause of this behaviour should probably be sought in the different nature of the hybridisation of the lone electron pairs of phosphorus and nitrogen.

Table 10. Comparison of the dipole moments of aliphatic and aromatic phosphines.

Compound	Dipole moment	References	Dipole moment	References
CH_3PH_2	1.100, gas	68	—	—
$C_6H_5PH_2$	1.11, hexane	129	—	—
$(CH_3)_3P$	1.192, gas	70		—
$C_6H_5P(CH_3)_2$	1.31, hexane	129	1.22, cyclohexane	127
$(C_2H_5)_3P$	1.45, benzene	121	1.48, benzene	128
$C_6H_5P(C_2H_5)_2$	1.45, benzene	129	1.40, dioxan	133
$(C_6H_5)_2PC_2H_5$	1.46, dioxan	133	1.35, cyclohexane	127
$(C_6H_5)_3P$	1.49, benzene	128	1.44, cyclohexane	127
$(C_4H_9)_3P$	1.49, benzene	128		
$C_6H_5P(C_4H_9)_2$	1.45, hexane	129		

The problem arises whether systems with phosphorus-(III) are possible in which $p-\pi$ conjugation in the ground state plays an appreciable role and whether there are methods whereby it can be observed. A sufficiently clear-cut answer cannot at present be given. If the above method of estimation of the nature of the hybridisation of orbitals from the valence angles yields the correct information about the valence state of phosphorus despite the assumptions made, one may postulate that such cases should occur. According to an estimate, the lone electron pair in tertiary amines has approximately 50% of p character. If such a pair is conjugated with a powerful electron-accepting substituent, the energy of $p-\pi$ interaction can also be appreciable. One cannot exclude the possibility that such conjugation would be reflected in the chemical or physical properties of the compound.

Goetz and coworkers[133,134] measured the dipole moments of substituted arylphosphines of the type p-$XC_6H_4P(C_6H_5)_2$ and p-$XC_6H_4P(C_2H_5)_2$. It was found that the observed dipole moments are usually higher than the values calculated assuming additivity. In the case of electron-donating substituents (methoxy- and dimethylamino-groups) this is evidence of $p_\pi-d_\pi$ conjugation, since $p-\pi$ conjugation may be postulated for halogens. It is remarkable that the differences between the observed and calculated dipole moments of diphenyl-p-methoxyphenyl- and p-dimethylaminophenyl-phosphines proved to be significantly greater than for their oxides and sulphides: the $p_\pi-d_\pi$ conjugation in the oxides and sulphides must be considerably more pronounced than in the phosphines. We may note that the observed and calculated dipole moments of tri-(p-chlorophenyl)-phosphine are identical. According to the data of other workers[136], the dipole moment of cyanodiphenylphosphine also agrees with the value calculated assuming additivity. Possibly the above differences between the observed and calculated dipole moments are not associated with $p-\pi$ conjugation but with other factors, in particular the imperfection of the model chosen for the calculations.

§ Using the high dipole moments of trialkylphosphines quoted by Klages and Langpape[127], Hudson[41] concluded that the lowering of the dipole moment on passing to aromatic phosphines is due to $p-\pi$ conjugation. This conclusion is open to objection, since the data of Klages and Langpape were not confirmed.

Thus one cannot at present give a definite answer to the question of the possible $p-\pi$ conjugation in systems with electron-accepting substituents posed above.

B. CHEMICAL AND PHYSICOCHEMICAL PROPERTIES

The study of the directive influence in electrophilic substitution in the benzene ring constitutes a classical chemical procedure for the investigation of the electronic effect of the substituent. Unfortunately this method cannot be applied to phosphorus(III) compounds because of the high nucleophilicity of phosphorus(III) itself, which leads to preferential attack of the electrophilic agent on the phosphorus atom. Nucleophilic substitution in aromatic phosphorus compounds is so far unknown. The only example of a direct investigation of the directive influence of phosphorus(III) is that of the nucleophilic addition of vinyl derivatives of phosphorus(III) to a double bond. It was in fact first employed for this purpose.

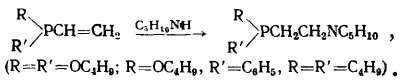
The electronic effect of groups with phosphorus(III) is investigated mainly by physicochemical methods, whereby it is possible to elucidate the nature of the resonance effects by indirect procedures. At the present time there exist two different approaches. The first of these is associated with the study of the effect of phosphorus(III) on the properties of the functional groups in the same benzene ring. The use of correlation analysis methods, in particular the Hammett equation, permits an indirect determination of the nature of the directive effect of the substituent. Valuable information about the nature of the π-electronic effects of phosphorus(III) is provided by protophilic deuterium exchange in aromatic phosphines and a number of other chemical properties. The second approach is based on reactions in which phosphorus is the reaction centre. This involves the study of the effect of substituents at the phosphorus atom on the reactivity of the lone electron pair, which permits an assessment of its capacity for delocalisation (the basicity of phosphines, alkylation reactions, and the addition of sulphur).

1. Electronic Effects of Phosphorus(III) as a Substituent

a. Directive influence in the addition of piperidine to vinyl derivatives of phosphorus(III). According to their directive influence in reactions involving ionic addition to vinyl derivatives of the type $CH_2=CH-X$, the substituents X can be divided into two types: the first includes π-donor groups, which as a rule direct the ionic part of the reactant to the α-position in relation to the substituent and the second group includes electron-accepting groups directing the reactant to the β-position. Substances of the first type, for example alkyl vinyl ethers and vinylamines, show a greater tendency to combine with electrophilic agents; substances of the second type, for example acrylonitrile, combine more readily with nucleophilic agents.

Vinyl derivatives of phosphorus(V) are typical electrophilic systems and readily combine with nucleophilic agents. It has been shown[6-8,137,138] that in all cases of addition the reactant is directed to the β-position regardless of the nature of the group at the phosphorus atom.

It was found unexpectedly[6-8] that the same type of directive influence is characteristic also of the vinyl compounds of phosphorus(III), although their reactivity is much lower than that of the phosphorus(V) compounds. The addition of piperidine was observed only under the conditions of prolonged heating of the reactants at 140–160°C:



$(R=R'=OC_4H_9;\ R=OC_4H_9,\ R'=C_6H_5,\ R=R'=C_4H_9)$.

The most reactive are the esters of vinylphosphonous and phenylvinylphosphinous acids, which combine with piperidine in the absence of catalysts. Piperidine hydrochloride accelerates the reaction but does not alter the site at which the addition takes place. The replacement of both butoxy-groups by phenyl groups leads to a sharp decrease of the reactivity of the double bond: in the absence of a catalyst and even in the presence of an acid catalyst, the addition could not be achieved. In the case of the more electropositive dibutylphosphino-group, the addition under the influence of piperidine hydrochloride still takes place, possibly owing to the formation of dibutylvinylphosphine hydrochloride.

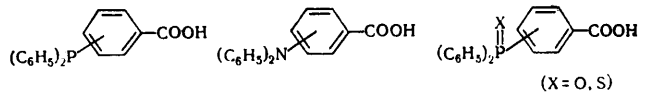
Thus, as regards the directive influence in the addition reaction, phosphorus(III) resembles silicon, which does not have a lone electron pair and for which a β-directing effect is also typical[139,140]. Later a β-directing effect was observed in the reaction of lithium diphenylphosphide with β-diphenylphosphinostyrene[141] and also in the reaction of butyl-lithium with vinylphosphines[142]. We may note that β-addition under the influence of a powerful nucleophilic agent such as butyl-lithium was also observed with phenyl vinyl sulphide[143]. Recently a β-directing effect was observed[144] in the addition of diphenylphosphine and diphenylarsine to vinyl- and ethynyl-phosphines in the presence of basic catalysts. The reaction of vinyl phosphorus(III) compounds with phenyliminobenzonitrile can be regarded as evidence in favour of a β-directing effect of substituents with phosphorus(III).[145,146]

The β-directing effect in the non-catalytic addition of piperidine is evidence either of the absence or of the insignificance of the π-donor effect in phosphorus(III). Its electron-accepting influence on the polarisation of the multiple bond or its stabilising effect on the transition state can be accounted for by $p_\pi-d_\pi$ conjugation and possibly by an inductive effect (since the electronegativities of H and P are the same and the inductive effect of the group will depend on the substituents at the phosphorus atom).

The data for the frequencies of the C=C stretching vibrations in the Raman spectra of vinyl and allyl derivatives of phosphorus(III) also agree with the conclusion that $p-\pi$ conjugation is absent[147]. A characteristic feature of $p-\pi$ conjugation—an increase in the integrated intensity of the double bond line, which is fairly distinct for the vinyl derivatives of nitrogen and sulphur and is not observed in vinylsilanes—is absent from the spectra. Vinyl derivatives of phosphorus(III) differ little from alk-1-enes as regards the spectroscopic effect of the double bond. Thus, according to both chemical and spectroscopic characteristics, vinyl compounds of phosphorus(III) are closer to vinylsilanes than to vinyl sulphides and vinylamines.

b. Effect of substituents with phosphorus(III) on the properties of functional groups in the benzene ring. For the investigation of the directive influence of phosphorus(III), indirect methods, in particular correlation analysis, have also been successfully employed. The authors of the present

review together with Lobanov[9,10,148] determined the ionisation constants of *m*- and *p*-diphenylphosphinobenzoic acids and for comparison the ionisation constants of *m*- and *p*-diphenylaminobenzoic acids and the corresponding benzoic acids containing groups with phosphorus(V):



(X = O, S)

The results are presented in Table 11. It was found that, regardless of the valence of phosphorus, all the phosphorus-containing substituents investigated increase the ionisation constant of benzoic acid and are therefore electron acceptors. Correspondingly Hammett's σ constants for phosphorus-containing substituents are positive.

Table 11. Ionisation constant (pK_a) of phosphorus-substituted benzoic acids XC_6H_4COOH and the σ, σ_I, and σ_R constants of the substituents X [1 : 1 (by volume) aqueous alcohol, 25°C].[9,10,148]

X	pK_a	$\frac{k_{meta}}{k_{para}}$	σ	$\sigma_p-\sigma_m$	σ_I	σ_R
H	5.72	1	0.00	0.00	0.00	0.00
p-$(C_6H_5)_2P$	5.39	0.76	0.19	0.08	0.05	0.14
m-$(C_6H_5)_2P$	5.51		0.11			
p-$(C_6H_5)_2N$	6.10	—	−0.29	—	—	—
m-$(C_6H_5)_2N$	5.77	2.18	−0.07	−0.22	0.11	−0.40
p-$(C_6H_5)_2P(O)$	4.88	—	0.53	—	—	—
m-$(C_6H_5)_2P(O)$	5.11	0.58	0.38	0.15	0.27	0.26
p-$(C_6H_5)_2P(S)$	4.97	—	0.47	—	—	—
m-$(C_6H_5)_2P(S)$	5.24	0.54	0.29	0.18	0.15	0.32

It is significant that *para*-phosphorus-substituted acids are stronger than the *meta*-substituted acids. This is evident from the ratios k_{meta}/k_{para}, which are less than unity, and also from the positive differences $\sigma_p - \sigma_m$, which are characteristic of *meta*-directing groups. Consequently all the phosphorus-containing substituents investigated are *meta*-directing. On the other hand, as was to be expected, the diphenylamino-group lowers the ionisation constant of benzoic acid to a greater extent when present in the *para*-position than when present in the *meta*-position and is thus an ortho-*para*-directing substituent.

The inductive (σ_I) and resonance (σ_R) components of Hammett's constants were calculated[148] from the constants σ_m and σ_p (Table 11). These values particularly clearly illustrate the nature of the electronic effect of substituents with phosphorus(III) and phosphorus(V). The inductive effect of the diphenylphosphino-group proved to be small, in agreement with the electronegativity of phosphorus. The groups with phosphorus(V) are of course characterised by larger inductive constants. The inductive effect of the diphenylamino-group exceeds that of the diphenylphosphino-group, which is consistent with the difference between the electronegativities of nitrogen and phosphorus (3.0 and 2.1 according to Pauling). The resonance effects of phosphorus-containing groups, particularly the diphenylphosphino-group, are interesting. It has been found that, in contrast to the diphenylamino-group, the diphenylphosphino-group is a π-electron acceptor despite the presence of a lone electron pair. The diphenylamino-group is a π-donor substituent, although its mesomeric effect is of course somewhat reduced compared with that of dialkylamino-groups. The resonance effects of substituents with phosphorus(V) are positive and exceed the resonance effect of the diphenylphosphino-group. These results permit an approximate estimation of the $p-\pi$ conjugation effect. The difference in the values of σ_R for the diphenylphosphino- and diphenylphosphinyl groups is caused, on the one hand, by the increase of the extent of $p_\pi - d_\pi$ conjugation owing to the presence of a positive charge at the phosphorus(V) atom and some compression of *d* orbitals and, on the other hand, by the absence of $p-\pi$ conjugation, which may occur in the case of phosphorus(III). We cannot estimate the contribution of each effect but the overall contribution, i.e. the difference between the values of σ_R for these groups, is very insignificant and amounts to only 0.12, which most probably indicates that the effect of $p-\pi$ conjugation is close to zero for the diphenylphosphino-group.

These results were later confirmed by other workers[16-29]. Unfortunately there is no information in the literature for *meta*-substituents with phosphorus(III) exception for the data quoted above. The results of Schiemenz[19,20] for phosphorus-containing groups in the *para*-position virtually agree with those obtained by ourselves. Somewhat different values of σ_p were found by Baldwin et al.[22] from the ionisation constants of phosphorus-substituted benzoic and arylphosphonic acids in aqueous tetrahydrofuran (THF). They are low for all phosphorus-containing groups. This may be associated with the effect of the solvent.

Table 12. Ionisation constants (pK_a) of phosphorus-substituted phenols XC_6H_4OH and the constants σ^-, σ_m, and σ_R^- of the substituents X [1 : 1 (by volume) aqueous alcohol, 25°C].[13,149-151]

X	pK_a	σ^-	σ_m (Refs.19 & 20)	σ	$\sigma^- - \sigma_p$	σ_R^-
H	11.21	0.00	0.00	0.00	0.00	0.00
p-$(C_6H_5)_2P$	10.46	0.26	0.32	0.19	0.07	0.16
p-$(C_6H_5)_2P(O)$	9.38	0.68	0.88	0.53	0.15	0.35
p-$(C_6H_5)_2P(S)$	9.49	0.63	0.73	0.47	0.16	0.44
m-$(C_6H_5)_2P$	10.82	—	—	0.12	—	—
m-$(C_6H_5)_2P(O)$	10.05	—	—	0.42	—	—
m-$(C_6H_5)_2P(S)$	10.14	—	—	0.38	—	—
p-$(CH_3)_2P$	10.67	0.18	—	—	—	—
p-$(CH_3)_2P(O)$	9.58	0.60	—	—	—	—
p-$(CH_3)_2P(S)$	9.58	0.60	—	—	—	—
m-$(CH_3)_2P$	10.90	—	—	0.09	—	—
m-$(CH_3)_2P(O)$	10.13	—	—	0.39	—	—
m-$(CH_3)_2P(S)$	10.02	—	—	0.43	—	—

Makhamatkhanov and the authors of the review[13,149-151] measured the pK_a of *meta*- and *para*-phosphorus-substituted phenols. Schiemenz measured the pK_a of *para*-phosphorus-substituted dimethylanilines[19,20]. The nucleophilic constants σ^- calculated from these data, which characterise the effect of electron-accepting substituents in the case of an electron-donating reaction centre, and the constants σ_m are listed in Table 12. These results differ somewhat from those of Schiemenz, probably owing to the difference in the reaction series¶. The σ^- constants for phosphorus-containing substituents are positive and exceed

¶ It is known that the constants σ^- are not universal and depend strongly on the nature of the reaction centre and the type of reaction.

the corresponding Hammett constants σ_p, which is evidence of an effect of the direct polar conjugation of the phosphorus-containing groups with the reaction centre. The difference $\sigma^- - \sigma_p$ for the diphenylphosphino-group is 0.07 in phenols and 0.13 in substituted dimethylanilines. Thus the electron-accepting effect of the direct polar conjugation of phosphorus(III) with the electron-donating reaction centre is small but distinct. The constants σ_m for phosphorus-containing groups, determined from the pK_a of the corresponding phenols and benzoic acids, agree satisfactorily among one another.

The constants σ^- and σ_m for the dimethylphosphino-group were found from the ionisation constants of dimethylphosphinophenols[150,151] (Table 12). They proved to differ little from the analogous constants for the diphenylphosphino-group.

Analogous results were obtained also for other reaction series. Thus positive albeit somewhat high values of σ_p for the diphenylphosphino-group (0.3 and 0.5) were derived from data for the reactivity of *p*-diphenylphosphinostyrene in copolymerisation with styrene and methyl methacrylate[152]. The constant σ_p for the diethylphosphino-group (0.03) was determined by Stepanov et al.[17] from the basicity of tetraethyl-*p*-phenylenediphosphine. The significant difference between this value and σ_p for the dimethylamino-group (−0.83) is noteworthy.

c. Electronic effect of substituents with phosphorus(III) according to data obtained by various physical methods. The electronic effect of phosphorus-containing groups was investigated by physical methods (infrared spectroscopy[18,19] and ^{13}C NMR, ^1H NMR, and ^{19}F NMR spectroscopy[23-32,153,154]) and in many cases the corresponding σ constants were determined. On the whole, these data agree with the results derived by chemical methods. The systematic study of the electronic effect of phosphorus-containing groups with the aid of ^{19}F NMR, undertaken by Taft and coworkers[27,38], Johnson and Jones[29], and also Schindlbauer and Prikoszovich[26,153,154], is of greatest interest. The σ constants which they found in many cases agree well with our data but the resolution into inductive and resonance components is somewhat different: according to ^{19}F NMR data, the σ_I constants are somewhat high and the resonance constants σ_R are low compared with the chemical results. It is noteworthy that the data of the above workers do not always agree with one another (Table 13). This is precisely why much importance cannot be attributed to the negative values of $\bar{\sigma}_R$ for the dimethylphosphino- and bis(dimethylamino)phosphino-groups. According to the results of a study of pentafluorophenyl phosphorus(III) compounds, dimethyl- and diphenyl-phosphino-groups are π-acceptor substituents[30-32] (see also other investigations[33-38]). ^1H NMR and ^{13}C NMR data for dialkylethynylphosphines also indicate a π-electron accepting effect of dialkylphosphino-groups[39,40]. Probably the problem of the exact estimation of the resonance and inductive effects of dialkylphosphino- and related groups with phosphorus(III) cannot be regarded as finally solved†, but it is already clear that the resonance effect of dialkylphosphino-groups is close to zero.

† For example, it is not clear why σ_I for the dimethoxyphosphino-group is smaller than for the dimethylphosphino-group (Table 13), since the opposite relations are observed for substituents with phosphorus(V).[143] The reason for the large value of σ_I for the dimethylphosphino-group compared with the bis(dimethylamino)phosphino-group is also obscure.

The ^1H NMR spectrum of triphenylphosphine indicates a small effect of the diphenylphosphino-group on the magnetic screening of the ring protons compared with benzene[155,156]. The type of spectrum changes from a singlet to a doublet depending on the solvent and the concentration of triphenylphosphine, which is evidence of a similarity of the chemical shifts of *o*-, *m*-, and *p*-protons[155]. On passing from deuterochloroform to hexadeuterobenzene, the spectrum is split and the signal of *o*-protons shifts by 0.09 p.p.m. towards weaker fields and those of *m*- and *p*-protons shift by 0.25 p.p.m. towards stronger fields, but the exact values of the chemical shifts have not yet been determined[156].

Table 13. The constant σ_I and $\sigma_{\bar{R}}$ of phosphorus-containing groups X_2P according to ^{19}F NMR data for phosphorus-containing fluorobenzenes.

X	σ_I		σ_R	
	Refs.27 & 28	Refs.26,153 & 154	Refs.27 & 28	Refs.26,153 & 154
H	—	+0.07	—	+0.17
CH_3	+0.06	+0.06	−0.06	+0.16
CH_3O	+0.16	—	+0.05	—
$(CH_3)_2N$	−0.05	—	−0.05	—
C_6H_5	+0.18	+0.21	0.00	+0.09
F	+0.39	—	+0.16	—
Cl	+0.43	+0.44	+0.16	+0.25
CF_3	+0.52	—	+0.16	—
CN	+0.58	—	+0.19	—

The ESR spectra of the radical-anions obtained from triphenylphosphine[157] and dimethylphenylphosphine[158] show that the diphenyl- and dimethyl-phosphino-groups are electron-accepting substituents according to their influence on the distribution of spin density‡. The ESR spectra of 2,6-di-t-butylphenoxy-radicals containing substituents with phosphorus(III) and phosphorus(V) in the 4-position lead to a similar conclusion[160].

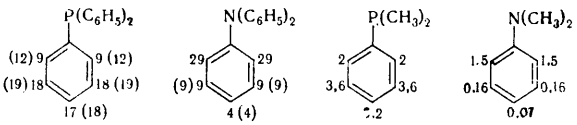
The different capacities of the lone electron pairs of nitrogen and phosphorus for resonance delocalisation are clearly shown in the mass spectra of the compounds of these elements. The principal fragment formed on electron impact from the bis(diphenylamino)methane molecule[161] is the resonance-stabilised cation $(C_6H_5)_2\dot{N}=CH_2$. The analogous diphosphinomethane gives rise to a more complex spectrum of fragments, among which species arising as a result of the migration of the phenyl group predominate: $C_6H_5\dot{P}\equiv CH$ and $(C_6H_5)_3\overset{+\cdot}{P}$. The $(C_6H_5)_2\dot{P}=CH_2$ fragment is formed in a smaller amount[161]. Comparison of the mass spectra of other phosphorus and nitrogen compounds lead to the same conclusions[162].

Thus physical methods confirm more or less convincingly the results of chemical studies.

d. Effect of substituents with phosphorus(III) on the rate of protophilic deuterium exchange in arylphosphines. It appears that at the present time one reaction involving the direct substitution of hydrogen in the benzene ring, under the directive

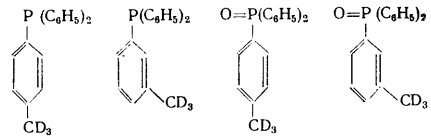
‡ Account must be taken of the fact that the formation of radical-anions from phosphines under the influence of metallic potassium in tetrahydrofuran is complicated by the cleavage of the phosphorus–carbon bond[159].

influence of phosphorus(III), is known, namely the metallation of diphenylphosphine by butyl-lithium, which results in a low yield (5.9%) of the *meta*-lithio-derivative[163]. Metallation of triphenylamine also leads to *meta*-substitution[164,165]. For a more detailed study of the effect of phosphorus-containing substituents on the reactivity of hydrogen atoms and methyl groups in the benzene ring, the authors of the review together with Yakovleva, Shatenshtein, and coworkers[14,167-169] investigated the kinetics of isotope exchange in deuterated triphenylphosphine, triphenylamine, dimethylphenylphosphine, and many other compounds. The partial rate factors for deuterium exchange (f) in liquid ammonia catalysed by potassamide or sodamide (the figures are quoted in brackets) are given below. The analogous data for dimethylaniline are included for comparison[170,171]:



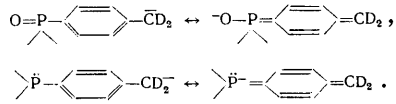
Comparison of the f_n for amines and phosphines indicates significant differences in the electronic effects of nitrogen and phosphorus: in the case of phosphorus the exchange is much faster than in the case of nitrogen. It is interesting that the approximate equality of the exchange rate constants for the *meta*- and *para*-positions of the ring is characteristic not only of phosphines but also of their oxides (1.2×10^{-6} and 0.8×10^{-6} in 1 : 1 t-butyl alcohol–diglyme in the presence of potassium t-butoxide at 120°C), which yet again indicates the similarity of the electronic effects of phosphorus(III) and phosphorus(V).

The electron-accepting properties of the diphenylphosphino-group are shown particularly clearly in the exchange involving the methyl groups of isomeric diphenyltolylphosphines:



(in 1 : 1 t-butyl alcohol–diglyme in the presence of potassium t-butoxide at 120°C).

The exchange rate constants quoted show that the exchange involving the *para*-methyl group is approximately 25 times faster than for the *meta*-methyl group. In the corresponding oxides the difference increases to a factor of 200. These data are evidence of the presence of π-acceptor conjugation in the carbanion or in the transition state arising in the exchange involving diphenyl-*p*-tolylphosphine and its oxide and probably having a structure similar to that of a carbanion:



Thus in the study of hydrogen exchange in aromatic and aliphatic phosphines it proved impossible to detect any signs of $p-\pi$ conjugation.

The electron-accepting properties of phosphorus(III) are observed[14] also when the relative rates of deuterium exchange in methyl groups attached to phosphorus and nitrogen atoms are compared, analogous relations being observed for oxygen and sulphur[172,173] (the exchange was carried out in liquid ammonia in the presence of potassamide, the rate of exchange involving the methyl group of toluene under the same conditions being adopted as a unit):

$C_6H_5N(CH_3)_2$	$(C_6H_5)_2NCH_3$	$C_6H_5OCH_3$
0.0001	0.0002	0.003
$C_6H_5P(CH_3)_2$	$(C_6H_5)_2PCH_3$	$C_6H_5SCH_3$
2	25	10000

2. Reactions Involving the Lone Electron Pair of Phosphorus(III)

The effect of substituents on the reactivity of the lone electron pair of phosphorus(III) has been inadequately investigated quantitatively. A more or less systematic study has been made only of the effect of substituents on the basicity of phosphines. The kinetic studies on the alkylation of phosphines and the addition of sulphur and phenyl azide are few and it is not always possible to arrive at any conclusions concerning $p-\pi$ conjugation.

a. Basicity of phosphines. The effect on this property of electronic and steric factors and of the hybridisation and hydration of the phosphonium cation has been discussed in fair detail by Hudson[41] and Arnett[174]. We shall deal only with problems concerning $p-\pi$ conjugation and shall consider certain studies which were not included in the above reviews.

When comparing the structure–basicity correlations for amines and phosphines, one is struck in the first place by the sharp difference in the effect of $p-\pi$ conjugation on the basicities of these two classes of compounds. During the last ten years a number of correlations have been proposed for amines in which account is taken of the effect on the basicity of electronic factors and solvation[175-179], the lowering of basicity owing to the conjugation of the unshared electron pair with the benzene ring being estimated as equivalent to approximately 3pK units (the agreement between the estimates of this quantity by different workers is not altogether satisfactory). A correlation for phosphines proposed by Henderson and Streuli[180] is analogous to Hall's first correlation for amines[175], where account is taken only of the inductive effects of substituents (Taft's σ^* constants). Tertiary, secondary, and primary phosphines give rise to three linear relations with similar slopes. It is interesting that, in contrast to aromatic amines, aromatic phosphines satisfy this relation. The deviations observed for certain arylphosphines (about 0.5pK unit) might be attributed to a slight $p-\pi$ conjugation, but the deviations are not always of the same sign and probably differ little from the average statistical scatter in the correlation. According to the data of Drenth and Hogervorst[181], the relations of Henderson and Streuli hold satisfactorily also for tertiary alkynylphosphines.

It was shown[182] that in the correlation of the pK_a for phosphines with the σ_{ph} constants for substituents at the phosphorus atom, primary, secondary, and tertiary phosphines give rise to a single linear relation, which is also satisfied by aromatic phosphines. If one remembers that, in terms of the system of σ_{ph} constants, the phenyl group is characterised by an electron-donor resonance effect[183] ($\sigma_I^{ph} = 0.27$, $\sigma_R^{ph} = -0.76$), it becomes clear that on protonation phosphorus in aromatic phosphines exhibits only electron-accepting properties and the lone pair probably does not interact with the π-electron systems of the benzene rings.

By potentiometric titration in nitromethane, Stepanov, Bokanov, and Korolev[16,17,184,185] determined the basicities of a number of ring-substituted diethylphenylphosphines [p-$XC_6H_4P(C_2H_5)_2$], including both electron-donating and electron-accepting substituents. The basicity of these compounds varies linearly with Hammett's σ-constants ($r = 0.9986$ and $s = 0.067$) but not with the σ^- constants, the latter relation being characteristic of substituted anilines. Hence it follows that the electronic effects in the protonation of phosphines are analogous to those in benzoate anions and in this sense differ fundamentally from the effects involving amines. These results also indicate the occurrence of $p_\pi - d_\pi$ conjugation in the protonated phosphine molecule and the insignificance (or absence) of the conjugation of the lone electron pair of the phosphorus atom with the aromatic ring in the molecule of the base.

Goetz and coworkers[186,187] investigated the basicity of phosphines of the same type and also substituted triarylphosphines [p-$XC_6H_4P(C_6H_5)_2$] in 80% alcohol. On the basis of analogous Hammett relations§, they concluded that both $p_\pi - d_\pi$ and $p - \pi$ conjugations occur in phosphines in the ground state. Since the substituents X were exclusively *ortho-para*-directing, the validity of the Hammett relation in this case is evidence only of acceptor conjugation but not of the delocalisation of the lone electron pair. However, on the whole the data for the basicities of substituted arylphosphines are not inconsistent with the hypothesis of the existence of a weak $p - \pi$ conjugation.

b. Alkylation of phosphines. Henderson and Buckler[188] investigated the kinetics of the alkylation of phosphines by alkyl halides. They found that the rate of reaction is determined mainly by inductive and steric factors, although in many cases there are exceptions which have not been fully accounted for. Trialkylphosphines with unbranched substituents (with the exception of the methyl group) and also triaryl and mixed alkylarylphosphines give an imperfect $\lg K - \Sigma\sigma^*$ linear relation, which can nevertheless be attributed to the absence or insignificance of the $p - \pi$ conjugation effect in aromatic phosphines.

c. Addition of sulphur and phenyl azide to aromatic phosphines. The addition of sulphur to substituted triphenylphosphines was investigated by Bartlett and Meguerian[189] and also Goetz et al.[190] The first group of investigators found for a small number of examples (with chlorine and methyl groups as substituents in the benzene rings) that the reaction is of second order and the rate constants are consistent with the Hammett equation (we may note that a similar relation obtains also when the σ^0 inductive constants are employed). Goetz and coworkers established that the reaction is not exactly of second order. Thus definite conclusions concerning the presence or absence of $p - \pi$ conjugation cannot be arrived at on the basis of these data. Nor can one reach conclusions about $p - \pi$ conjugation from studies on the kinetics of the addition of azides to substituted triphenylphosphines recently carried out by Leffler and Temple[191,192].

§ In the correlation of the basicities of aryldiethylphosphines Goetz and coworkers[187] employed averaged Jaffé constants and found that the points corresponding to Cl and Br deviated appreciably from the resulting straight line, to which the authors attributed fundamental importance. It is easy to show that, when McDaniel and Brown's σ constants are employed, a linear relation is obtained with a high correlation coefficient and applies to all the substituents.

C. PROPERTIES OF CERTAIN INDIVIDUAL TYPES OF COMPOUNDS

1. Carboxylic Acid Phosphides

The phosphides of carboxylic acids, containing the group $\diagup\!\ddot{P}-\underset{|}{C}=O$, constitute an interesting system. The presence of the polar carbonyl group and the lone electron pair creates more favourable conditions for $p - \pi$ conjugation than in the $\diagup\!\ddot{P}-\underset{|}{C}=C\diagdown$ systems. These compounds are analogues of carboxylic acid amides, in which there is a very pronounced conjugation of the lone electron pair with the carbonyl group. The study of the chemical and physical properties of carboxylic acid phosphides showed in many cases a difference from the properties of amides, which can probably be regarded as evidence of only a weak $p - \pi$ interaction in this system.

Like carboxylic acid amides, the corresponding phosphides exhibit appreciable acylating properties. According to the data of Tyka and Plazek[193,194], triaroyl phosphides on being heated for many hours with alcohols (140–160°C), give the corresponding esters in quantitative yields. The reaction with aqueous ammonia or aniline results in a quantitative formation of the corresponding amides. Monoacyl phosphides have analogous properties[195,196]. It is interesting that the reverse reactions do not take place. Probably the carbonyl group in phosphides is somewhat more reactive than in amides, but, as stated by Issleib and Priebe[195], there are no fundamental differences between phosphides and amides in this respect.

It is significant that, in contrast to amides, the lone electron pair of phosphorus in monoacyl phosphides retains its reactivity. Thus monoacyl phosphides yield methiodides and form complexes with salts of nickel, mercury, cadmium, and other heavy metals[196,197]. The ease of their oxidation (up to self-ignition) and the capacity to add sulphur and bromine are all evidence of the absence or insignificance of the delocalisation of the lone electron pair of phosphorus[196,197].

Interesting results were obtained in a study of the physical properties of carboxylic acid phosphides. According to Issleib and Löw[196], the ν_{CO} frequencies in amides and phosphides differ little from one another and lie in the range 1640–1680 cm^{-1}, i.e. are much lower than in ketones (Table 14). These results have also been confirmed by Kostyanovskii and coworkers[197-204].

Kostyanovskii and coworkers[197,202,204,205] found that, together with the band indicated above, the spectra of phosphides contain, in contrast to amides, a second band located at a frequency higher by approximately 100 cm^{-1}, which they also attributed to the stretching vibrations of the carbonyl group (Table 15). The presence of two bands was explained by the existence of two stable conformers, the low-frequency band being attributed to the *trans*-conformer (the *trans*-positions of the lone pair and the CO group) and the high-frequency band to the *cis*-conformer. The authors state that the relative intensities of these bands change as a function of the solvent and temperature. Since the conjugation of the lone electron pair and the carbonyl group cannot be achieved for geometrical reasons (the π-electron system of the carbonyl group and the orbital of the lone electron pair do not lie in the same plane), the authors explain the lowering of ν_{CO} by the conjugation of the carbonyl group with the phosphorus d orbitals, which leads to a lowering of the multiplicity of the C=O bond

owing to the reverse polarisation of the carbonyl group with the appearance of a positive charge at the oxygen atom.

$$\rangle\ddot{P}-C=O \leftrightarrow \rangle\ddot{P}=\bar{C}-O^{+}\cdot$$
(I) (II)

Table 14. Comparison of the ν_{CO} frequencies for amides and phosphides $RCOER'_2$ according to the data of Issleib and Löw[196].

Element	ν_{CO}, cm^{-1}			
	R = R′ = alkyl	R = alkyl, R′ = aryl	R = aryl, R′ = alkyl	R = R′ = aryl
N	1655	1680	1645	1655
P	1650	1670	1640	1655

This treatment is open to objection. The relative contribution of structure II with the unusual polarisation of the carbonyl group to the resonance system should be very small and the insignificant reverse polarisation of the bond, which on the whole has a certain amount of semipolar character ($\bar{C}-\bar{O}$), should lead to an increase and not to a decrease of the amount of double bond character in the carbonyl group and hence to an increase of ν_{CO}. If it is assumed that the multiplicity of the C=O bond is reduced owing to structure (II), then the factors promoting the reverse polarisation should lead to a further decrease of ν_{CO}. Nevertheless ν_{CO} in phosphorus(V) systems of the type $RCOP(O)R'_2$ and $[RCO\dot{P}R'_2R''X^-]$, where both inductive and mesomeric effects should stabilise resonance structure (II), is higher and not lower.

Table 15. Variation of ν_{CO} in mono- and di-acetophosphides and acetamides[197,202,204].

Formula	ν_{CO}, cm^{-1}		
$CH_3COP(CH_3)_2$	1660	—	1758
$(CH_3CO)_2PCH_3$	1657	—	1758
$CH_3COP(C_6H_5)_2$	1664	—	1758
$CH_3CON(CH_3)_2$		1650	
$(CH_3CO)_2NCH_3$		1700	
$CH_3CON(C_6H_5)_2$		1662	

The decrease of ν_{CO} in amides is due to $p-\pi$ conjugation, which leads to a lowering of the multiplicity of the C=O bond. At first sight it may appear that the lowering of ν_{CO} in phosphides is due to the same phenomenon, but this is contradicted by other chemical and physical data which indicate the absence or insignificance of $p-\pi$ conjugation in systems with phosphorus(III).

For an understanding of the causes of the lowering of ν_{CO} in carboxylic acid phosphides, it is useful to examine the variation of ν_{CO} in carbonyl-containing compounds of the type CH_3COX, where X are atoms or groups containing elements in Pe iods II and III (Fig. 6 and Table 16). One must bear in mind that ν_{CO} does not depend significantly on the mass of the substituents[210] (provided that the mass exceeds 12) and therefore ν_{CO} is determined mainly by electronic factors. For example, it has been shown that ν_{CO} is sensitive to the inductive effects of substituents[211,212].

On passing from carbon to nitrogen, ν_{CO} falls approximately by 60–90 cm^{-1} despite the higher electronegativity of nitrogen, which is due to $p-\pi$ conjugation¶. On further transition to oxygen and fluorine, there is a steady increase of ν_{CO} in conformity with the increase of the inductive and the decrease of the mesomeric effects of these elements. On passing from carbon to silicon, which has a lower electronegativity, ν_{CO} decreases and it was shown that in this case the decrease is caused by a change in the inductive effect of the substituent and not by other factors.

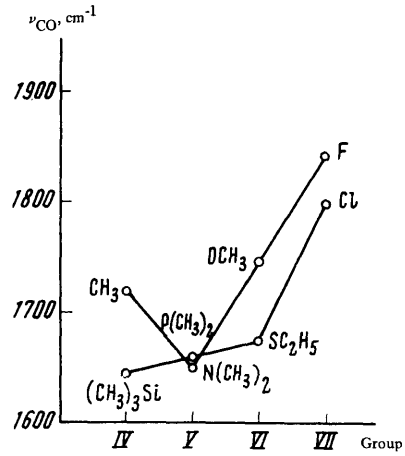


Figure 6. Variation of ν_{CO} in CH_3COX molecules, where X are substituents containing Group IV–VII elements in the Second and Third Periods.

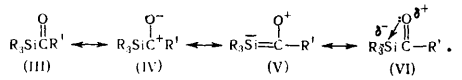
Table 16. Variation of ν_{CO} in CH_3COX molecules (in the condensed phase of solution).

X	ν_{CO}, cm^{-1}	References	X	ν_{CO}, cm^{-1}	References
CH_3	1718	206	$Si(CH_3)_3$	1645	208
$N(CH_3)_2$	1650	204	$P(CH_3)_2$	1660, 1758	197,201
OCH_3	1747	206	SC_2H_5	1675	209
F	1841	207	Cl	1798	207

In α-silyl-substituted ketones ν_{CO} is reduced approximately by 70 cm^{-1} compared with ν_{CO} in the corresponding ketones without the α-silyl group[208,214–218]. In disilyl-substituted ketones an even greater shift is observed[219]. The replacement of the α-carbon atom of ketones by silicon has a surprisingly powerful effect also on the energy of the electronic transitions[215,218,219], leading to a red shift of the bands in the ultraviolet spectrum and the appearance of a colour in α-silyl-substituted (yellow) and disilyl-substituted (red-violet) ketones, which is not

¶ In amides, where $p-\pi$ conjugation cannot be achieved for geometrical reasons, ν_{CO} does not fall. Thus ν_{CO} = 1756 cm^{-1} for 2,2,6-trimethyl-7-quinuclidone[213].

observed in the ketones having similar structures without the silyl groups. To account for these observations, it was suggested that the lone electron pair of the oxygen atom in the carbonyl group interacts with the silicon *d* orbitals ($n-d$ interaction[215]) and it was postulated that in the excited state the π^* orbitals of the carbonyl group are conjugated with the silicon *d* orbitals[220]. The possible electronic interactions in silyl-substituted ketones can be represented by a set of resonance structures[221] (III–VI):



(III) (IV) (V) (VI)

Examination of this problem with the aid of the simple and extended Hückel methods led to the conclusion[222] that the main reason for the observed influence of silicon and also germanium on the electronic and vibrational spectra is the change in the σ-donor capacity of the substituting α-atom†. This view was confirmed by spectroscopic measurements of the basicity of the carbonyl group in $R_3XCOC_6H_5$.[221] The basicity decreases in the series Si > Ge > C, which is evidence against structures (V) and (VI) in the ground state. Thus it has been shown that the electronegativity of silicon, i.e. its inductive and not mesomeric effect, plays the main role in the changes of ν_{CO}.

For other elements of Period III, with the exception of phosphorus, a lowering of ν_{CO} in the system CH_3COX, analogous to that with silicon, is observed and one may assume that it is caused by a decrease of the inductive effect of X, since the decrease of the mesomeric effect, which takes place on passing to the elements of the Third Period, should lead to an increase of ν_{CO}. This general tendency does not hold only in the case of phosphorus: ν_{CO} in phosphides is reduced compared with ν_{CO} in ketones but not amides. Compared with silicon, there is some increase of ν_{CO} instead of a decrease, as in the case of carbon and nitrogen. One may suppose that the decrease of ν_{CO} for phosphides compared with ketones is caused, by analogy with silicon, by a decrease of electronegativity on passing from carbon to phosphorus and the approximate equality of the ν_{CO} for phosphides and amides is associated with the absence or insignificance of the $p-\pi$ conjugation effect in carboxylic acid phosphides. Issleib and Löw[196] believe that the reason for the decrease of ν_{CO} in phosphides is the polarisability and reduced electronegativity of phosphorus compared with nitrogen.

Two absorption bands, assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition, have been observed in the ultraviolet spectra of phosphides[197,202,204] (Table 17). Compared with amides, which have only one band associated with the $\pi \rightarrow \pi^*$ transition, a bathochromic shift of the absorption maximum should be noted, although it is not as pronounced as in the case of silyl-substituted ketones. A colour is observed only for the phosphides of aromatic and heterocyclic carboxylic acids. The reason for the bathochromic shift is probably the reduced electronegativity of phosphorus.

The introduction of a second acyl group at the phosphorus atom has little effect on the vibrational and electronic spectra (Tables 15 and 17), while in the case of nitrogen a second acyl group increases ν_{CO} and the bathochromic shift in the ultraviolet spectrum[202]. This is associated with a change in the nature of the conjugated system in diacyl derivatives of nitrogen and probably with the absence of $p-\pi$ conjugation in diacyl phosphorus compounds.

Thus the sum total of all the data considered probably indicates the absence from phosphides of $p-\pi$ conjugation analogous to the amide resonance.

Table 17. Ultraviolet spectra of phosphides[197,202,204] and amides[202,224].

Formula	λ, nm (in hexane)		Formula	λ, nm (in hexane)	
	$\pi \rightarrow \pi^*$	$n \rightarrow \pi^*$		$\pi \rightarrow \pi^*$	$n \rightarrow \pi^*$
$CH_3COP(CH_3)_2$	228.5	347.0	$CH_3CON(CH_3)_2$	195.3	—
$(CH_3CO)_2PCH_3$	220.5	342.0	$(CH_3CO)_2NCH_3$	215.7	—

2. Phosphorus(III) Cyanides

From the standpoint of the conditions for the occurrence of $p-\pi$ conjugation, the $\diagdown\ddot{P}-C\equiv N$ system is more favourable than the $\diagdown\ddot{P}-C=O$ structure. In this case there is no conformational limitation to conjugation. In the discussion of valence angles it was already noted that the C–P–C valence angle in tricyanophosphine is 93.5°, which corresponds to almost complete *s* character of the lone electron pair of phosphorus and hence the absence of capacity for $p-\pi$ conjugation. Therefore the study of the properties of such compounds is of great interest for the conjugation problem.

The chemical properties of phosphorus(III) cyanides have been hardly investigated. Michaelis[225] pointed out that aryldicyanophosphines add chlorine vigorously. Cyanodiphenylphosphine adds sulphur on interaction with $PSCl_3$. Tricyanophosphine forms complexes[227] with aluminium hydride and also with aluminium chloride and bromide. These reactions indicate the retention of reactivity by the lone electron pair despite the powerful inductive effect of the cyano-groups.

As already mentioned, the dipole moment of cyanodiphenylphosphine does not differ from the value calculated assuming additivity[136], which is evidence of either the absence or low contribution of $p-\pi$ conjugation in the molecule. This is consistent also with the vibrational spectra of tricyanophosphine. A correlation[228] between $\nu_{C\equiv N}$ and the electronegativity of the element has been established for the cyanides of various elements. The cyanides of elements with lone electron pairs (fluorine, chlorine, bromine, iodine, and sulphur) give rise to a single linear relation and elements incapable of $p-\pi$ conjugation (carbon, mercury, silicon, and potassium) form another straight line. It is interesting that phosphorus is included among the second group of elements, while sulphur is included among the first. The authors emphasise this finding, which is surprising in their opinion.

The lowering of $\nu_{C\equiv N}$ in phosphorus(III) cyanides compared with alkyl cyanides is probably not caused by conjugation but by the reduced electronegativity of the phosphorus atom. The changes in $\nu_{C\equiv N}$ in $X-C\equiv N$ systems, where X are elements in the Second and Third Periods, are analogous to those described above for the carbonyl compounds CH_3COX (Fig. 7 and Table 18).

† The interaction of the π bond of the carbonyl group with the silicon *d* orbitals is postulated in the excited state[223].

3. Phospholes

The problem of the aromaticity of five-membered phosphorus-containing heterocycles, the so called phospholes, which are the phosphorus analogues of pyrrole, furan, and thiophen, bears a direct relation to problems of $p-\pi$ conjugation.

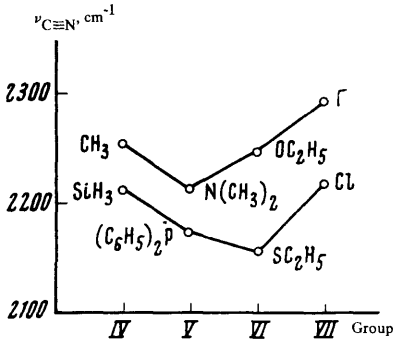


Figure 7. Variation of $\nu_{C\equiv N}$ in X–C≡N molecules, where X are substituents containing Group IV–VII elements in the Second and Third Periods.

A number of polyphenyl derivatives of phospholes were synthesised at the beginning of the 1960's [236-242]. Recently simple representatives of this class of compounds were obtained: 1-phenylphosphole [243] and 1-methylphosphole [244,245]. The study of these compounds [238-241,245-247] showed that, in contrast to aromatic heterocycles, they combine the properties of dienes and saturated compounds of the heteroatom, i.e. phosphines. Phospholes enter into all the reactions characteristic of phosphorus(III) compounds: they are oxidised, add sulphur, and give rise to quaternary phosphonium salts and complexes. On the other hand, pentaphenylphosphole, for example, behaves as a diene forming an adduct with maleic anhydride [238,239].

Table 18. Variation of $\nu_{C\equiv N}$ in XC≡N molecules (in the condensed phase of solution).

X	$\nu_{C\equiv N}$, cm^{-1}	References	X	$\nu_{C\equiv N}$, cm^{-1}	References
CH_3	2254	229	SiH_3	2212 (gas)	233
$N(CH_3)_2$	2212	230	$P(C_6H_5)_2$	2172	136
			$P(CN)_2$	2204	228
OC_2H_5	2245	231	SC_2H_5	2155	234
F	2230 (gas)	232	Cl	2215	235

Tetraphenylthiophen and tetraphenylfuran do not form analogous adducts even under severe conditions. Pentaphenylphosphole forms complexes with iron carbonyls both via the phosphorus atom and via the diene system [238,239]. 1,2,5-Triphenylphosphole forms two types of adduct with acetylenedicarboxylic acid ester—as a diene and as a phosphine with formation of phosphoranes [248].

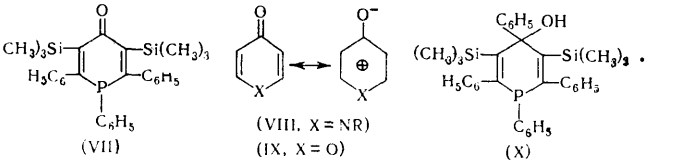
Some evidence for aromaticity was obtained in the study of the simplest phospholes. Thus Märkl and Potthast [243] state that 1-phenylphosphole does not dimerise at 20°C, in contrast to its oxide, and is comparatively difficult to oxidise and combine with sulphur to form a dimeric oxide and sulphide. The NMR spectrum of 1-phenylphosphole resembles that of 1-phenylpyrrole. Quin and coworkers [244,245] enumerate a number of properties, which in their opinion indicate a significant degree of delocalisation of the lone electron pair in 1-methylphosphole: the higher stability of the phosphole compared with that of dienes; the shift of the proton signals in the NMR spectrum towards weaker fields, indicating the existence of a ring current and a similar shift of the signals of the methyl protons; the indication by the ^{31}P NMR spectrum of a reduced electron density at the phosphorus atom compared with alkyldivinylphosphines; the similarity of the ultraviolet spectrum to that of 1-methylpyrrole; the fragmentation on electron impact similar to that of pyrrole and thiophen derivatives; a basicity (0.5) lower by approximately five powers of ten than the expected basicity of methyldivinylphosphine; the absence of reactions with carbon disulphide and nickel chloride. On the other hand, 1-methylphosphole is readily oxidised and forms a phosphonium salt with methyl iodide, which suggests the retention of the reactivity of the lone electron pair of the phosphorus atom. Thus the available data do not allow a final conclusion concerning the presence or absence of aromatic properties in phospholes. However, even if phospholes do exhibit aromatic properties, they are weak and they do not have a significant influence on the overall properties of these heterocycles.

We may note that thermochemical and calculated quantum-chemical data support the existence of aromatic properties in phospholes. According to these results, described in fair detail in Hudson's book [41], phospholes should actually have more pronounced aromatic properties than pyrroles, a result which must naturally be treated with caution‡.

There are no data on the geometry of phospholes. Earlier we pointed out that [12] the valence angles at the heteroatoms in pyrrole, furan, and thiophen are approximately equal to those in the hydrides of the corresponding elements. If this holds also for phosphorus, the valence angles at the phosphorus atom in phospholes should differ only slightly from those in unsubstituted phosphine, i.e. they should not exceed 100° in any case. The predominantly *s* character which the lone electron pair possesses in this case is in good agreement with the absence of pronounced aromatic properties in phospholes.

4. Phosphacyclohexadienones

Märkl and Olbrich [249] recently synthesised 3,5-trimethylsilyl-1,2,6-triphenylphosphacyclohexa-2,5-dien-4-one (VII), the phosphorus analogue of γ-pyridone (VIII) and γ-pyrone (IX), which are known to have aromatic properties owing to the delocalisation of the lone electron pair of the heteroatom X over the ring:



‡ A planar ring structure was postulated in the calculation.

The phosphacyclohexadienone (VII) does not exhibit the ambident reactivity characteristic of pyrones and pyridones. Thus alkylation and protonation take place at the phosphorus atom and not at the oxygen atom. Compound (VII) enters into reactions characteristic of phosphorus(III) and ketones. The carbinol (X) obtained in the reaction with phenyl-lithium does not form with perchloric acid the corresponding pyrylium salt analogue. All these properties indicate the absence of appreciable delocalisation of the lone electron pair of the phosphorus atom in the phosphacyclohexadienone, although the authors in fact believe that the involvement of the dipolar structure probably should not be entirely excluded.

We shall not consider here the problem of phosphabenzenes, since the lone electron pair of phosphorus does not participate in the conjugated ring system.

V. PROPERTIES OF PHOSPHORUS(III) COMPOUNDS IN AN OPTICALLY EXCITED STATE

A. ULTRAVIOLET SPECTRA OF PHOSPHINES

Examination of the ultraviolet spectra of the simplest chromophoric systems with lone electron pairs of the type CH_3X, where X is a substituent containing elements in Groups V–VII and Periods II and III, shows that the position of the long-wavelength absorption band is inversely related to the electronegativity of the central atom of the substituent X: with increase of the electronegativity of the central atom, the long-wavelength absorption band is displaced towards shorter wavelengths (Table 19). There is a corresponding increase in the excitation energy, which is attributed either to $n \rightarrow \sigma^*$ transitions or, as in some cases, to Rydberg transitions of an electron from lone pair[257-259]. Within the limits of the Second Period, there exists an approximate linear relation between the position of the absorption band and the electronegativity of the central atom (see lines I and II in Fig. 8*a*). On passing from the elements of the Second Period to those of the Third in Groups VI and VII, the absorption bands are displaced towards longer wavelengths (see lines I and II in Fig. 8*b*), in conformity with the decrease of the electronegativity of the elements. However, in Group V the opposite phenomenon is observed—phosphines absorb at shorter wavelengths than amines, which leads to a breakdown of linearity. Thus phosphorus is an exception to the general relation. One may suppose that this blue shift, i.e. the increase of the energy of the long-wavelength transition, in phosphines is associated largely with the lower and not the excited energy level of the lone electron pair, i.e. with the enhanced *s* character of its orbital.

If phosphorus satisfied the above relation, then, according to its electronegativity (2.1 on Pauling's scale), the long-wavelength transition of trimethylphosphine should occur in the region of 240–260 nm instead of the observed wavelength of about 200 nm. The energy difference between the 200 and 250 nm transitions[102] is approximately 28 kcal mole^{-1}. Table 19 lists the parameters of the ultraviolet spectra of other phosphines and, for comparison, data for the corresponding amines. In all cases the long-wavelength transitions of phosphines are displaced towards shorter wavelengths compared with amines, which can probably be regarded as confirmation of the conclusion that the lone electron pair of phosphorus has enhanced *s* character.

Analogous, albeit less pronounced, changes in the position of the long-wavelength absorption bands are also observed for monophenyl derivatives[260-262] (Figs. 8*a* and 8*b*). In this case the long-wavelength transition is of a different type, although the attached element with a lone pair has a significant influence on the nature of the spectrum. The maximum of the long-wavelength absorption band is displaced towards shorter wavelengths on passing from nitrogen to oxygen and fluorine, i.e. on increase of the electronegativity and decrease of the π-donor capacity of the element.

Table 19. Long-wavelength absorption bands of chromophoric systems with lone electron pairs.

Substance	λ_{max}, Å	Solvent	References	Substance	λ_{max}, Å	Solvent	References
NH_3	1942	gas	250	PH_3	1910	gas	253
CH_3NH_2	2150	ditto	250	CH_3PH_2	2010	ditto	253
$(CH_3)_2NH$	2200	»	250	$(CH_3)_2PH$	1890	»	253
$(CH_3)_3N$	2273	»	250	$(CH_3)_3P$	2010	»	253
$(CH_3)_2O$	1840	»	251	$(CH_3)_2S$	2100	alcohol	254
CH_3F	1325	»	252	$(C_2H_5)_2S$	2222	gas	255
				CH_3Cl	1690	gas	256

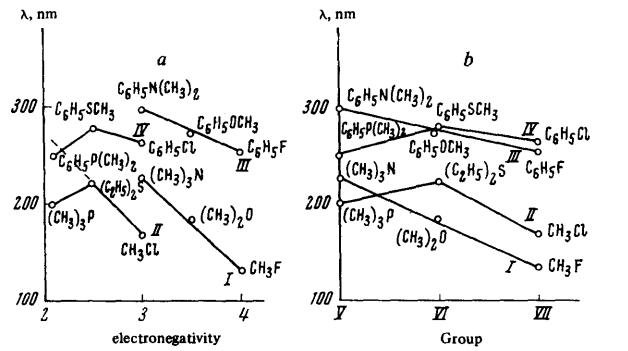


Figure 8. Variation of the positions of the long-wavelength absorption band maxima in the spectra of compounds of the type CH_3X and C_6H_5X (X are substituents with lone electron pairs containing Group V–VII elements in the Second and Third Periods) with Pauling's electronegativity of the central atom of the group X (*a*) and with the positions of the central atom in the Periodic System (*b*).

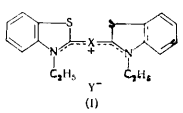
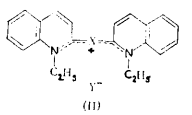
A small bathochromic shift is observed on passing from fluorine to chlorine and from oxygen to sulphur. Again this behaviour breaks down in the case of phosphorus (see Figs. 8*a* and 8*b* and Table 20). According to the general tendency, phosphorus compounds should be characterised by absorption at the longest wavelengths. In fact, however, dimethylphenylphosphine absorbs at shorter wavelengths than the analogous nitrogen and sulphur compounds and, according to the data of Bowden and Braude[261], even fluorine compounds, despite the lower electronegativity of phosphorus compared with those of the above elements. This anomaly in the spectra indicates a significant difference in the structure of the valence shell of phosphorus in

phosphines and possibly also a different type of electronic transition. One may suppose that it is also caused by enhanced *s* character of the lone electron pair of phosphorus.

Table 20. Long-wavelength absorption bands of the monophenyl compounds of certain elements in the Second and Third Periods (in alcohol).

Substance	λ_{max}, nm	References	Substance	λ_{max}, nm	References
$C_6H_5N(CH_3)_2$	309 298	260 261	$C_6H_5P(CH_3)_2$	266.0 251.0	260 261
$C_6H_5OCH_3$	273	260	$C_6H_5SCH_3$	279.0	261
C_6H_5F	254	261	C_6H_5Cl	263.5	260

Table 21. Ultraviolet spectra of cyanine dyes.

Formula	X	Y	λ_{max}, nm	References
 (I)	N	BF_4	376 (CH_3OH)	263
	CH	I	423 (CH_3OH)	263
	P	BF_4	472 (CH_3OH)	263
			478 (C_2H_5Cl)	264
	As	BF_4	491 (C_2H_5Cl)	264
 (II)	N	I	424	268
	CH	I	525	269
	P	ClO_4	5 4 (CH_3OH)	263
	As	BF_4	642 (C_2H_5Cl)	264

It is interesting to note that in those cases where tervalent dicoordinate phosphorus enters into a conjugated system, anomalies of this kind are not observed in the spectra and phosphorus compounds absorb at longer wavelengths than the analogous nitrogen compounds. Thus the phosphamethinecyanines synthesised by Dimroth and Hoffmann[263] have a deeper colour than the corresponding azamethine- and methine-cyanines (Table 21). The analogous arsenic compounds absorb at even longer wavelengths[264]. An approximately linear relation is actually observed between the position of the long-wavelength absorption band maximum and the electronegativity of the central atom (Fig. 9). A bathochromic shift of the long-wavelength absorption maximum relative to the maxima of the corresponding carbon and nitrogen analogues takes place also for other compounds of dicoordinate phosphorus – dibenzophosphorin[265] and 2,4,6-triphenylphosphabenzene[267,269].

Aryl phosphide anions[41], the electronic analogues of aryl sulphides and arenethiols, are also deeply coloured. The appearance at the phosphorus atom of a second lone electron pair with a much more pronounced *p* character than the first leads to a shift of the absorption band towards longer wavelengths in accordance with the electronegativity of phosphorus.

The first data on the ultraviolet spectra of aromatic phosphines were obtained at the beginning of the 1950's. Extensive data have now been accumulated but so far the nature of the observed electronic transitions is not altogether clear.

The introduction of phosphorus(III) into the benzene ring leads to a sharp increase of the absorption intensity in the region of 250–260 nm, which exceeds the usual increase of intensity accompanying the breakdown of the symmetry of the benzene ring, and also to a bathochromic shift of the benzene *K* band. This was first shown by Bowden and Braude[261] for dimethylphenylphosphine and then by other workers[134,135,260,270-276] for other aromatic phosphines. An increase in the number of phenyl groups at the phosphorus atom causes a comparatively small change in the position of the absorption band but leads to an appreciable increase of intensity, which, however, does not rise in proportion to the number of benzene rings[260,271].

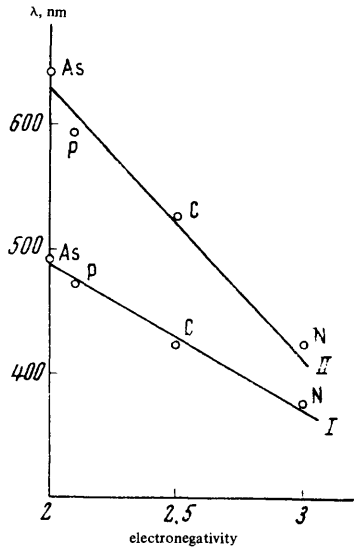


Figure 9. Variation of the positions of the maxima of the long-wavelength absorption bands in the spectra of cyanine dyes of types I and II (Table 21) with Pauling's electronegativity of the central atom.

This effect is shown particularly clearly by aromatic amines. The band intensities are influenced by steric factors. Thus the introduction of a methyl group into the *ortho*-position of 1-phenyl-1-phosphacyclopentane decreases the intensity of the long-wavelength band[270] although not as much as for dimethylaniline[279]. The intense absorption in the region of 250–260 nm is associated with the lone electron pair of phosphorus(III), since this band disappears in the oxidation or formation of phosphonium salts. In phosphorus(V) compounds a low-intensity band with a vibrational fine structure is observed in the same region. We may also note that in phosphorus(V) derivatives there is no progressive increase of intensity on introduction of benzene rings at the phosphorus atom and the rule of additivity holds[271,272].

All these factors are regarded by some workers as evidence for the occurrence of $p-\pi$ conjugation in aromatic phosphines in the ground state. Thus Jaffé[271,272] believed that the ultraviolet spectra of the triphenyl derivatives of Group V elements in the tervalent state indicate

the existence of powerful conjugation between the benzene rings§. This view was supported also by Rao and coworkers[274,275], who assigned the 260 nm band of triphenylphosphine initially to the $n \rightarrow \pi^*$ transition and then to the $\pi \rightarrow \pi^*$ transitions, i.e. to the modified benzene B band, and regarded it as an analogue of the long-wavelength absorption by triphenylamine (297 nm). A similar assignment was made by Schindlbauer and coworkers[276,277], who discussed the spectra of more complex aromatic phosphines. Schiemenz[278] believes that the principal bands in the spectrum of di(cyanoethyl)phenylphosphine and cyanoethyldiphenylphosphine are similar to those associated with the long-wavelength transition of dimethylaniline, although in the case of triphenylphosphine he refrains from a definite assignment of the long-wavelength absorption.

Cullen and coworkers[280,281] stated that triphenylamine is the sole representative of triphenyl derivatives of Group V elements whose benzene rings are conjugated. The spectra of the remaining compounds of the series differ significantly from that of triphenylamine. By mathematical analysis of the spectroscopic data for arylarsines, these workers isolated two long-wavelength maxima, one of which was assigned to the $\pi \rightarrow \pi^*$ electronic transition of the substituted benzene ring on the basis of the influence of solvents and substituents on its position and the other (the principal intense absorption band) was assigned to the $n \rightarrow \pi^*$ transition. This investigation influenced also the interpretation of the ultraviolet spectra of arylphosphines.

Table 22. Ultraviolet spectra of arylphosphines[155].

Formula	$n \rightarrow \pi^*$ transition		$\pi \rightarrow \pi^*$ transition	
	λ_{max}, nm	ϵ	λ_{max}, nm	ϵ
$C_6H_5P(C_2H_5)_2$	252.6	3300	273.2	140
$(C_6H_5)_2PC_2H_5$	251.3	8090	277.8	950
$(C_6H_5)_3P$	261.4	11000	281.7	1250

Shaw et al.[155] made a similar analysis of the ultraviolet spectra of arylphosphines with different numbers of phenyl groups at the phosphorus atom (Table 22). They assigned the principal intense band with a maximum in the region of 250–260 nm to the $n \rightarrow \pi^*$ transition of an electron from the lone pair to a non-bonding orbital of the benzene ring. The low-intensity bands with maxima in the region of 270–280 nm were assigned to the $\pi \rightarrow \pi^*$ transitions of the electrons in the substituted benzene ring. These bands differ little in their positions and intensities from the long-wavelength bands of monosubstituted benzenes, for example toluene[282]: 269 nm (2.4), 262 nm (2.45), 255 nm (2.3), and 249 nm (2.15). This interpretation is equivalent to the acknowledgement of the absence (or insignificance) of $p-\pi$ conjugation in the ground state and the delocalisation of the lone electron pair in the optically excited state. The problem of the presence or absence of weak $p-\pi$ conjugation in the ground state remains open. Shaw and coworkers believe that such weak conjugation is possible in triphenylphosphine on the basis of the long-wavelength displacement of the band associated with the $\pi \rightarrow \pi^*$ transition. The recently published spectra of mono-, di-, and tri-phenylphosphines in the gas phase[283] are interesting in this respect. The spectral curve for triphenylphosphine has a shoulder in the region of 300–310 nm.

A similar interpretation was made by Stepanov and coworkers[184,185] in an examination of the ultraviolet spectra of substituted aryldiethylphosphines. On the basis of the effect of substituents in the aromatic ring and at the phosphorus atom on the position of the absorption maximum, they concluded that the intense long-wavelength band of phosphines is an *R* band ($n \rightarrow \pi^*$ transition) and the $\pi \rightarrow \pi^*$ transition is in the majority of cases masked by this intense absorption.

The interpretation of the long-wavelength band as due to the $n \rightarrow \pi^*$ transition is consistent with the enhanced *s* character of the lone electron pair of phosphorus, and hence with the absence or insignificance of $p-\pi$ conjugation in the ground state and with the physical and chemical properties of aromatic compounds; it explains the "phosphorus" anomaly in the spectroscopic behaviour described above.

The assignment to the $n \rightarrow \pi^*$ transition was made[284] also for the long-wavelength band in the spectra of vinylphosphines in the region of 230–240 nm and the 260–270 nm band for *trans*-diphosphinoethylenes. The absorption in the region of 180 nm observed previously[147] probably refers to the unperturbed band of the $\pi \rightarrow \pi^*$ transition, which usually undergoes a bathochromic shift in the spectra of vinylamines and vinyl sulphides. However, we may note that the above assignments are so far purely qualitative and have not been confirmed by calculations.

B. MOLECULAR REFRACTIONS OF PHOSPHORUS(III) AROMATIC COMPOUNDS

Without considering the problem of the molecular refractions of organophosphorus compounds as a whole, which was recently examined in detail by Tolkmith[285] and partly by other investigators, we shall deal here only with a specific problem—the exaltation of the molecular refractions (ΔMR_D) of aromatic phosphorus(III) compounds. In recent years Kharrasova and Kamai examined the molecular refractions of aromatic phosphorus(III) compounds[290-294].

The replacement of an alkyl group at the phosphorus atom by a phenyl group is always accompanied by the exaltation of molecular refraction, which is regarded as evidence for the conjugation of the lone electron pair of phosphorus with the π-electron system of the benzene ring. ΔMR_D is not constant and depends on the substituents at the phosphorus atom and in the benzene ring and their positions.

The values of ΔMR_D for the simplest mono- and diphenyl compounds of phosphorus(III) are listed in Table 23. In most cases it was compiled using the results of the present authors. For this reason, the ΔMR_D data presented serve merely as an illustration and are not increments to atomic refractions of phosphorus. The smallest exaltations are observed for primary and secondary phosphines and chlorophosphines. When alkyl, alkoxy-, and dialkylamino-groups are introduced at the phosphorus atom, ΔMR_D gradually increases and in the case of the last two groups these value differ significantly from the ΔMR_D for chlorophosphines¶. The introduction of a

§ Subsequently Jaffé apparently abandoned this treatment[273] and stated that the absorption by triphenylphosphine in the region of 260 nm cannot be definitely attributed either to the *B* or *K* band.

¶ Kharrasova and Kamai state[291] that the replacement of chlorine by an alkoxy-group in aromatic compounds of phosphorus(III) does not alter its atomic refraction.

second phenyl group increases the exaltation by 0.5–0.7 cm^{-3}. For triphenylphosphine[299], ΔMR_D = 2.65 cm^3.

The exaltations of disubstituted aromatic compounds (Table 24) depend on the nature of the substituents and their positions in the benzene ring. For *meta*-isomers, ΔMR_D differs only significantly from the sum of the ΔMR_D for the corresponding mono-substituted compounds, whereas for the *para*-isomers they are significantly higher than this sum. In other words, ΔMR_D increases with increasing length of the conjugation chain. The above dependence of ΔMR_D on structure makes it significantly more difficult to devise an additive scheme for the calculation of the molecular refractions of aromatic phosphorus(III) compounds.

Table 23. Exaltation of the molecular refractions of certain mono- and di-phenyl compounds of phosphorus(III) [$C_6H_5PX_2$ and $(C_6H_5)_2PX$].

X	$C_6H_5PX_2$	References	$(C_6H_5)_2PX$	References
H	0.48[a]		1.07[b]	
Cl	0.50	296, 297	1.27[c]	
CH_3	0.77	14	1.26	14
OR	1.20	298	1.83[d]	291
$N(C_2H_5)_2$	1.37[e]		2.08	291

[a]Data of the authors of the review: $C_6H_5CH_2$—b.p. 50–51°C/18 mmHg, n_D^{20} = 1.5812, d_4^{20} = 0.9944; MR_D: found 36.86, calculated 36.38. AR_p (8.97) calculated from the MR_D for primary phosphines with straight-chain alkyl substituents. The constants were taken from Maier's review[295].

[b]Data of the authors of the review: $(C_6H_5)_2PH$—b.p. 120–121°C/4 mmHg, n_D^{20} = 1.6293, d_4^{20} = 1.0744; MR_D: found 61.55, calculated 60.48. AR_p (8.97) calculated from the MR_D for secondary phosphines with straight-chain alkyl substituents. The constants were taken from Maier's review[295].

[c]Data of the authors of the review: $(C_6H_5)_2PCl$—b.p. 141–142°C/5 mmHg, n_D^{20} = 1.6367, d_4^{20} = 1.1904; MR_D: found 66.46, calculated 65.19.

[d]Calculated from MR_D for $(C_6H_5)_2POR$ only.

[e]Data of the authors of the review: $C_6H_5P[N(C_2H_5)_2]_2$—b.p. 121–122°C/4 mmHg, n_D^{20} = 1.5344, d_4^{20} = 0.9731; MR_D: found 80.67, calculated 79.30.

Recently Zaitsev[305] proposed correlation equations for the calculation of ΔMR_D for disubstituted benzenes. As experimental data accumulate, this scheme can probably be used also for organophosphorus compounds.

The absolute values of the above exaltations are fairly high and comparable with those for aromatic amines. However, in order to compare the exaltations of phosphorus and nitrogen compounds, it is probably more reasonable to employ, instead of the absolute value of ΔMR_D, its ratio to the corresponding atomic refraction, which makes it possible to take into account the different polarisabilities of the elements. This ratio, which may be called the relative exaltation, is analogous to the specific refraction of Auwers and Eisenlohr[306] but is more convenient for comparing the analogous compounds of various elements.

The relative exaltations for aromatic phosphines are smaller by a factor of approximately 3 than for aromatic amines. Thus, as regards the breakdown of the additivity of molecular refractions, it would appear that phosphorus(III) compounds may be regarded as typical conjugated systems, although inferior in this respect to aromatic amines. The problem arises of the reliability of the exaltation of molecular refraction as a criterion of the occurrence of conjugation.

Table 24. Exaltation of the molecular refractions of *para*- and *meta*-substituted monophenyl compounds of phosphorus(III).

Compound XC_6H_4Y	ΔMR_D p-XC_6H_4Y	References	ΔMR_D m-XC_6H_4Y	References
$ClC_6H_4PCl_2$	1.10	300	0.67	301
$ClC_6H_4P(C_4H_9\text{-}n)_2$	1.48	300	1.20	301
$ClC_6H_4P(OC_2H_5)_2$	1.56	300	1.31	301
$ClC_6H_4P[N(CH_3)_2]_2$	1.98	300	1.59	301
$NCC_6H_4PCl_2$	1.94	9	1.26	10
$NCC_6H_4P(C_4H_9\text{-}n)_2$	2.94	148	1.98	148
$CH_3OC_6H_4P(CH_3)_2$	1.24	303	0.94	303
$CH_2{=}CHC_6H_4P(OC_2H_5)_2$	2.94	304	—	

Compound XC_6H_4Y	ΔMR_D XC_6H_5	References	ΔMR_D C_6H_5Y	$\Delta MR_D XC_6H_5 + \Delta MR_D C_6H_4Y$
$ClC_6H_4PCl_2$	0.03	302	0.50	0.53
$ClC_6H_4P(C_4H_9\text{-}n)_2$	0.03	302	0.85*	0.88
$ClC_6H_4P(OC_2H_5)_2$	0.03	302	1.20	1.23
$ClC_6H_4P[N(CH_3)_2]_2$	0.03	302	1.37	1.40
$NCC_6H_4PCl_2$	0.83	302	0.50	1.33
$NCC_6H_4P(C_4H_9\text{-}n)_2$	0.83	302	0.85*	1.68
$CH_3OC_6H_4P(CH_3)_2$	0.31	1	0.77	1.08
$CH_2{=}CHC_6H_4P(OC_2H_5)_2$	1.16	1	1.20	2.36

*Data of the authors of the review: $C_6H_5P(n\text{-}C_4H_9)_2$—b.p. 112–113°C/4 mmHg, n_D^{20} = 1.5245, d_4^{20} = 0.9159; MR_D: found 74.34, calculated 73.49.

According to Vol'kenshtein[307], "static exaltation, extrapolated to infinitely long wavelengths, i.e. zero frequencies, is of physical significance". Then the breakdown of the additivity of molecular refractions may be evidence of conjugation in the ground state of the molecule. When the wavelength of the irradiating light is reduced, the exaltation will increase as the irradiation frequency approaches the frequency of the intrinsic absorption by the substance. For example, according to the data of Vasil'ev[308], at infinitely long wavelengths *p*-nitroaniline has an exaltation of 2.7 cm^3, which indicates the occurrence of conjugation in the ground state. The exaltation at 4358 Å reaches 14.85 cm^3. The increase of exaltation is due to the absorption of energy and the transition of some of the molecules to an optically excited state, where the additivity of molecular refractions found from the increments for the ground state should not hold. Certain exaltations are due precisely to this effect and are not associated with conjugation in the ground state. No data are available on the dispersion of the exaltations of molecular refractions for arylphosphines. One cannot exclude the possibility that in this case the exaltations are associated with the intrinsic absorption by the substance and on extrapolation to infinite wavelengths the molecular refractions will be additive. This is confirmed indirectly by the virtual absence of exaltation from vinyl compounds of phosphorus(III),[147] the intrinsic absorption bands of which are displaced towards shorter wavelengths[284].

Recently Zaitsev[309] demonstrated the existence of an approximate correlation between ΔMR_D and the electronic absorption spectra of monosubstituted benzenes.

Thus the exaltation of the molecular refractions of aromatic amines by itself gives no information about the conjugation in the ground state of these molecules. Nor should one forget $p_\pi - d_\pi$ conjugation as a possible cause of exaltation in certain cases.

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The properties of phosphorus(III) compounds discussed, both physical and chemical, have been explained on the hypothesis of an enhanced *s* character of the lone electron pair of phosphorus and to some extent constitute its confirmation. We may note that the nature of the hybridisation of the lone electron pair is fairly rarely taken into account in discussions of $p-\pi$ conjugation†, even in certain quantum-chemical studies[283,312]. Usually it is postulated that any lone electron pair is capable of $p-\pi$ conjugation to some extent, which depends on the position of the element in the Periodic System. Much attention has been devoted to the dependence of conjugation on steric factors (various types of non-coplanarity of the *p*-orbital axes), while the effect of changes in valence angles and of the hybridisation of the lone electron pair is rarely taken into account, although it is known that the *s* orbital does not form a bond with the p_Z orbital[45]. We believe that the chemistry of phosphorus(III) has shown that the hybridisation of the lone electron pair is a significant factor influencing the $p-\pi$ conjugation and the properties associated with it. Probably the geometry of the molecule always affects the conjugation not only because of a change in the relative distribution of the overlapping orbitals but also via a change in the very nature of the orbitals and the suggested hypothesis is probably more general and of wider significance than for the chemistry of phosphorus alone.

The problem naturally arises whether it is possible to predict on this basis cases in the chemistry of other elements where the lone electron pair of the atom loses the capacity for $p-\pi$ conjugation by virtue of its enhanced *s* character. The necessary conditions for the observation of this effect are the presence of only one lone electron pair and the closeness of the valence angles at the heteroatom to 90°C. On the basis of data for the valence angles in the hydrides of various elements (see p. 181, Table 1), one may note in what cases the absence of the capacity for $p-\pi$ conjugation in the lone electron pair of the atom is to be expected.

A sharp decrease of valence angles is observed on passing from elements in the Second Period to those in the Third Period within the limits of Groups V and VI. As shown above, in Group V this change in angles is accompanied by a change in directive influence. Since the valence angles in the hydrides of arsenic and antimony steadily decrease, approaching 90°, one may suppose that the lone electron pairs of these elements will also lack the capacity for $p-\pi$ conjugation. In Group VI, transition from the Second to the Third Period is not accompanied by a change in the type of directive influence of the central atom owing to the presence of two lone electron pairs. However, in the case of the tricoordinate state of Group VI elements, for example in 'onium compounds, the pattern of the changes in directive influence should be the same as in Group V elements. An analogous change in directive influence may also be expected for the tricoordinate state of Group IV elements, i.e. in the case of their anions, and the anions of silicon and its analogues should differ sharply in their electronic influence from carbanions.

The experimental data for certain properties (the type of directive influence of the central atom, basicity, and configurational capacity) of π-electron systems containing Group IV–VI elements in the tricoordinate state were recently examined by the present authors[313]. They agree with the hypotheses put forward. Here we shall recall only studies dealing with problems of directive influence and certain others which had not been dealt with previously.

Together with Lobanov, Kamai, and Chadaeva, the authors of the review[314] showed that arsenic, the closest analogue of phosphorus in the Group, resembles the latter in its electronic influence and its lone electron pair also lacks the capacity for $p-\pi$ conjugation. This is also indicated by the data of Kostyanovskii and coworkers[315].

It is interesting that the 100% *para*-directing effect in the nitration of a triphenyloxonium salt, which is unusual for 'onium compounds, observed by Nesmeyanov and coworkers[316] follows logically from the proposed hypothesis. The change in the type of directive influence on passing from oxonium to sulphonium salts is analogous to the inversion of directive influence on passing from nitrogen to phosphorus. Triphenyloxonium salts are electronic analogues of triphenylamine and probably have similar molecular geometry and hence their lone electron pair is almost entirely of *p* type‡. The lone electron pair of triphenylsulphonium salts, the electronic analogues of triphenylphosphine, probably has an appreciable amount of *s* character and hardly participates in $p-\pi$ conjugation. Finally, one must also bear in mind *d* orbitals with likewise promote the *meta*-directing effect. A similar *meta*-directing effect is observed with selenonium salts[317].

Some data whereby the hypotheses put forward may be checked are provided by five-membered diene heterocycles. Anionic cyclic systems containing Group IV elements should not have aromatic properties with the exception of the cyclopentadienide anion, which is derived from an element of the Second Period. The same applies also to Group V elements, nitrogen being an exception in this case. Group VI elements, which have two lone electron pairs, should all form aromatic heterocycles without exception. In the tricoordinate state, the same Group VI elements will not form aromatic heterocycles, with the exception of oxygen.

The facts known at present do not contradict the above hypotheses. We shall not dwell on the widely known examples of aromatic heterocycles—pyrrole, furan, thiophen, selenophen, and the cyclopentadienide anion. According to the hypotheses, the ring compounds with sulphur(III) (thiophen oxide), which is an unstable reactive diene, has no aromatic properties, although it does have a lone electron pair[318]. In this respect, the study of oxonium salts of furan, which should be aromatic, is of very great interest. As already stated, phospholes do not have very marked aromatic properties. However, one may assume that, in the form of phosphide anions, phospholes will behave as aromatic systems analogous to the

† These problems are partly dealt with in monographs[102,310] and certain papers[75,311].

‡ The *meta*-directing effect observed in the nitration of 2-phenylpyrylium salts[3] is not inconsistent with the *para*-nitration of triphenyloxonium salts, since in the first case the lone electron pair is probably located in the plane of the aromatic ring and is not conjugated with the benzene ring.

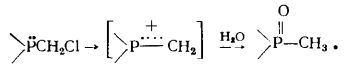
cyclopentadienide anion. The study of the silacyclopentadienide anion, the silicon analogue of the cyclopentadienide anion, has so far not provided a definite answer to the question of its aromaticity[319].

Another range of phenomena is closely associated with the problems discussed. Indirect evidence for the geometry of silicon(III) [Si (IV) tricoordinate Si? (Ed. of Translation)] compounds and hence for the type of directive influence of the negatively charged atom is provided by the inability of silicon to form a double bond[320]. We believe that this demonstrates the closeness of the valence angles in tricoordinate silicon compounds to 90°, the predominantly s character of the free silicon orbital, and hence the absence of $p-\pi$ conjugation in these systems (positively or negatively charged).

The forced decrease of the valence angles of carbon and nitrogen leads to analogous phenomena. This concerns all cases associated with Bredt's rule—the impossibility of the existence of double bonds or resonance interactions at the bridgeheads of bicyclic systems: the absence of amide resonance from quinuclidones[321] and the much lower basicity of dehydroquinuclidine and analogous compounds compared with the corresponding saturated compounds[322,323], the absence of resonance stabilisation from bicyclic carbanions with the charge at the bridgehead[324], etc. The impossibility of π-electron interactions in all such cases is due not only to the unfavourable geometrical disposition of the corresponding orbitals, which is usually emphasised, but also to the enhanced s character of the orbital at the bridgehead. The closeness of the average valence angle at the bridgehead in bicycloheptane systems to 100° has been pointed out by Sim[325].

Returning to phosphorus, we may note that the problem of the possibility of detecting $p-\pi$ conjugation in certain special cases is of great interest. We believe that there are three ways whereby phosphorus(III) systems may be formed in which $p-\pi$ conjugation is possible: (1) optical excitation of molecules; (2) the formation of a cationic centre in the α-position relative to phosphorus(III): (3) a "forced" change in the valence angles of the phosphorus atom by the introduction of bulky substituents or by the formation of cyclic structures.

Analysis of the ultraviolet spectra of aromatic phosphines leads to the extremely reasonable conclusion that in an optically excited state $p-\pi$ conjugation may occur. Its observation requires a study of the properties of optically excited molecules. One cannot exclude the possibility that the presence in the molecule of a powerful electron-accepting centre, for example a carbonium ion, leads to the delocalisation of the lone electron pair of phosphorus(III). Evidence for this is provided by the study of the reaction of tri(chloromethyl)phosphine which we investigated[326]:



Hydrolysis and reaction with alkoxides lead to the reduction of the chloromethyl group and the oxidation of phosphorus(III) and not simple substitution. This reaction, which we called "pseudoallyl rearrangement", probably indicates some delocalisation of the lone electron pair in the transition state.

The third way, involving a change in the valence angles at the phosphorus atom, has at present not been investigated at all, although isolated data show that the desired results may be obtained by this procedure. Mark and van Wazer[327] showed that the lone electron pair of tri-t-butyl phosphite has an enhanced reactivity, which they explained by an increase of the valence angles and of the p character of the lone electron pair. Subsequently this was confirmed[328] by the ^{31}P NMR method. Arbuzov and Zoroastrova[329], who synthesised a number of cyclic phosphites, noted that seven- and eight-membered phosphorochloridites ignite spontaneously in air, in contrast to the remaining members of the series. This finding has received no explanation. If one bears in mind that, according to X-ray diffraction data[330-335], the valence angles in 8–12-membered rings exceed the tetrahedral value (for example, in cyclononylamine hydrobromide[331] the C–C–C angles are in the range 111–124°), this anomaly can be understood. Probably an increase in the valence angles at the phosphorus atom leads to an increase in the amount of p character of the lone electron pair and an increase in its reactivity.

ADDENDA

During the preparation of this manuscript for the press, certain studies were published which the authors feel it necessary to include in the review. Wherever possible the additional data were introduced into the main text. In addition, three new small sections have been written, supplementing the sections on "The Basicity of Phosphines", "Phospholes", and "The Properties of Certain Individual Types of Compounds".

The barrier to the inversion of 1-isopropyl-2-methyl-5-phenylphosphole[336], determined by the NMR method, proved to be very low (ΔG_{25} = 16 kcal mole^{-1}), in contrast to tertiary phosphines for which the inversion barrier is 29–36 kcal mole^{-1}. The authors explain the lowering of the barrier by the energy gain due to the delocalisation of electrons in the transition state of the inversion process.

Proton Affinity of Unsubstituted Phosphine in the Gas Phase

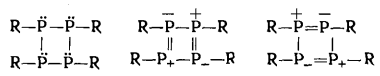
In contrast to ammonia, amines, and substituted phosphines, unsubstituted phosphine is known[41,174] to have an extremely low basicity in water (pK_a = −8 or −14), which Gibbs[337] explained by the almost complete s character of the lone electron pair of phosphorus and hence high rehybridisation energy from the p^3 to the sp^3 state in the phosphonium cation. On the basis of calculations using the Born–Haber cycle, Wendlandt[338] concluded that, despite the low accuracy of the values obtained, in the gas phase ammonia and phosphine differ little in their proton affinity (proton affinity is understood as the enthalpy, with the sign reversed, of the reaction $B + H^+ = BH_4^+$).

This led to another view, according to which the low basicity of unsubstituted phosphine in water is a consequence of the low solvation energy of the phosphonium ion[41,338,339]. Subsequently new estimates of the proton affinity of unsubstituted phosphine were published[340,341] (153 and 194.4 kcal mole^{-1}), which differed from Wendlandt's results (209 kcal mole^{-1}). According to the latest data[342] obtained by ionic cyclotron resonance, the proton affinity of unsubstituted phosphine is 185 ± 4 kcal mole^{-1}, which is smaller by 22 kcal mole^{-1} than the proton affinity of ammonia[343] (207 ± 3 kcal mole^{-1}). This value is comparable with the difference between the basicities of phosphine and ammonia in water (23–32 kcal mole^{-1}). Hence

it follows that solvation probably does not play a major role in the difference between the basicities of unsubstituted phosphine and ammonia in water.

Conjugation in Compounds with a P–P Bond

The problem of the possible aromatic properties of cyclopolyphosphines $(RP)_n$ (n = 4, 5, or 6) owing to the delocalisation of the electrons in the lone pairs of the phosphorus atoms and represented by the resonance structures



has been discussed in the literature[344,345]. This hypothesis was put forward[346,347] to account for the long-wavelength absorption in the ultraviolet spectra of cyclopolyphosphines (275–290 nm for alkyl derivatives), which is absent from the spectra of tertiary phosphines, and also for the low basicity of cyclopolyphosphines[347] ($pK_a < 1$) compared with phosphines ($pK_a = 2-10$). To confirm this treatment of the ultraviolet spectra, a quantum-chemical calculation was carried out[346].

Analogous evidence (ultraviolet spectra[348,349] and dipole moments[350]) was adduced in support of the existence of a partial double bond character in diphosphines in the ground state and certain polyphosphine heterocycles[351]. Some chemical properties of polyphosphines have also been explained[344,345,352] by the conjugation of the lone electron pair of phosphorus with the d orbitals of an adjacent phosphorus atom.

The valence angles at the phosphorus atom have been determined for trifluoromethyl[353,354], phenyl[355,356], and cyclohexyl[357] derivatives of tetra- and penta-phosphines. In most cases they do not exceed 100°. This implies that the lone electron pairs of phosphorus atoms are predominantly of s type and their conjugation with the d orbitals of phosphorus (the formation of a π bond) can hardly influence significantly the properties of cyclopolyphosphines in the ground state. We believe that the observed long-wavelength shift can be due both to $p_\pi - d_\pi$ conjugation in the optically excited state and to differences between the properties of the P–P (polyphosphines) and C–P (tertiary phosphines) σ bonds i.e. the difference between the electronegativities of carbon and phosphorus (see the section "Carboxylic Acid Phosphides"). The operation of the latter factor is supported, in particular, by the bathochromic shift in the ultraviolet spectra of diphosphine disulphides[349] (compared with trialkylphosphine sulphides), which cannot be accounted for by conjugation. The low basicity of cyclopolyphosphines may be associated with the enhanced s character of the lone electron pairs of phosphorus. The approximate equality of the P–P bond lengths, which are independent of the valence state of phosphorus and of the nature of groups attached to it[357], is also evidence against conjugation in the ground state.

Recently, in a discussion of the causes of the weak nucleophilic properties of the lone electron pair of phosphorus in trisilylphosphine, the hypothesis was put forward[358] that the lone s electron pair of phosphorus forms a σ bond with the d orbital of silicon located along the Si–P bond axis (for example the $s-d_{Z^2}$ σ bond). The hypothesis of additional σ bonding, rather than the π bonding, discussed above, may serve as an alternative explanation of the properties of compounds with a P–P bond.

Thus the properties of polyphosphines may be understood in terms of hypotheses other than that of $p_\pi - d_\pi$ conjugation in the ground state, which is difficult to reconcile with the extensive experimental data on the properties of phosphorus(III) compounds§.

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§ Added in proof. The weaker nucleophilic properties of the lone electron pair of phosphorus in triethyl phosphorothioite can be understood similarly; the hypothesis of the d hybridisation of the lone electron pair of phosphorus was recently put forward to account for it[361].

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Reactions of Organic Derivatives of the Elements with Polyhalogenomethanes

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The review discusses the reactivity of organic derivatives of the elements (with one or two "non-organic" atoms) in relation to halogenomethanes. The chemical reactivity of true organic derivatives of elements in Groups I-V in reactions with alkyl halides is determined by the type of the compound and the nature of the element-carbon bond. Particular attention has been devoted to initiated processes.
The bibliography includes 250 references.

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I. INTRODUCTION

Extensive empirical data have now accumulated on reactions of organic derivatives of the elements (ODE) with polyhalogeno-derivatives of methane. These reactions are of definite theoretical interest and are employed in organic syntheses.

The reactivity of ODE depends on the type of compound and the nature of the element and the organic group bound to the atom of the element. Some ODE react with polyhalogenomethanes at a low temperature and others only on heating, irradiation with ultraviolet light, or in the presence of initiators. The sharp differences between the reactivities of ODE and the use of different conditions in studies on the reactions are frequently the reasons for the contradictory interpretation of the mechanism of the reaction of ODE with polyhalogenomethane.

The literature dealing with the reactions of true organic compounds of Group I–V elements with polyhalogenomethanes is critically examined in this review in order to be able to discuss the mechanisms of these processes, their general characteristics, and the general relations governing them.

II. REACTIONS OF ORGANOMETALLIC COMPOUNDS OF GROUP I ELEMENTS

The reactions of organometallic metallic compounds (OMC) of Group I elements with polyhalogenomethanes have been investigated in greatest detail for lithium derivatives. Organolithium compounds react vigorously with di-, tri-, and tetra-halogenomethanes in hydrocarbon, ether, or tetrahydrofuran (THF) solutions at a low temperature (between −100° and −60°C). The greatest number of communications deal with reactions of compounds of the type RLi (R = CH_3,[1-6] iso-C_3H_7,[1,7] n-C_4H_9,[8-12] s-C_4H_9, t-C_4H_9, n-C_5H_{11},[2] cyclo-C_6H_{11},[10] C_6H_5,[13,14] and substituted vinyl[15,16]) with methylene dichloride. The main products of the reaction are lithium chloride and saturated and unsaturated cyclopropane hydrocarbons and their chloro-derivatives.

It has been shown[12] that dichloromethyl-lithium is formed as an intermediate:

$$RLi + CH_2Cl_2 \rightarrow RH + CCl_2HLi\ .$$

The presence of a dichloromethyl derivative in the reaction mixture was confirmed by reactions with mercury(II) chloride and zinc chloride, which led to the isolation of bis(dichloromethyl)mercury (m.p. 154–155°C) in almost quantitative yield and bis(dichloromethyl)zinc, which is stable at room temperature.

Dichloromethyl-lithium is an unstable compound, which decomposes above −60°C. There is no unanimous view concerning the mechanism of its decomposition. Arguments are quoted in favour of a bimolecular decomposition[12]:

$$2Cl_2HCLi \rightarrow 2\ LiCl + ClCH{=}CHCl\ .$$

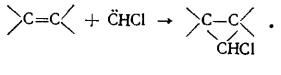
However, the majority of investigators postulate the participation of free chlorocarbene in reactions of organolithium compounds with methylene dichloride:

$$Cl_2CHLi \rightarrow LiCl + \ddot{C}HCl,$$

which makes it possible to account for the presence in the reaction mixture of many of the compounds formed.

Insertion or addition reactions are most characteristic of carbenes and a number of monographs[17,18] and reviews[19-21] have been devoted to them.

The reaction of organolithium compounds with methylene dichloride in the presence of olefins[4-6,9,22] leads to the formation of chlorocyclopropanes in high yields:



This reaction may be employed for preparative purposes. Chlorocarbene reacts with benzene, phenol[23], pyrrole, and indole[24] with ring expansion and adds to triphenylphosphine[25] with formation of ylide.

Chlorocarbene is inserted in the C–Li bond of the initial organometallic derivative with formation of a substituted chloromethyl-lithium derivative[10,14]:

$$R{-}Li + \ddot{C}HCl \rightarrow RCHClLi .$$

The decomposition of the latter gives rise to alkyl- or aryl-carbenes:

$$RCHClLi \rightarrow LiCl + R\ddot{C}H$$

(R = alkyl[8,10] or aryl[13,14]).

Alkylcarbenes tend to undergo intermolecular isomerisation, which leads to the formation of olefins and cyclopropanes. Thus the reaction of pentyl-lithium with methylene dichloride in ethyl ether solution at –30°C or in pentane solution at 30°C results in the formation of hex-1-ene (94–95%)† and n-propylcyclopropane (5–6%) owing to the isomerisation of the pentylcarbene formed initially. The principal products isolated in the analogous reactions of s-butyl-lithium and t-butyl-lithium are 2-methylbut-1-ene, ethylcyclopropane and *trans*-dimethylcyclopropane for the first compound and 2-methylbut-1-ene, 2-methylbut-2-ene, and 1,1-dimethylcyclopropane for the second[10].

In contrast to alkylcarbenes, arylcarbenes[13,14] undergo telomerisation or recombine to form symmetrical diarylethylenes (30–34%).

In the reaction of organolithium compounds with methylene dibromide, a bromine atom and not a hydrogen atom is split off from the latter:

$$RLi + CH_2Br_2 \rightarrow RBr + CH_2BrLi \rightarrow \ddot{C}H_2 + LiBr .$$

The carbene adds to olefins[4,26,27] or is inserted in the carbon–metal bond of the organometallic compound taken in excess[28]. Bromobenzene (25%), benzyl bromide (21%), and dibenzyl (37%) were isolated from the reaction mixture of phenyl-lithium[29] with methylene dibromide. In the reaction of methyl-lithium[30] with methylene dibromide the products are methyl bromide (5%), ethyl bromide (48%), and propyl bromide (13%):

$$RLi + \ddot{C}H_2 \rightarrow RCH_2Li ,$$

$$RCH_2Li + \ddot{C}H_2 \rightarrow RCH_2CH_2Li ,$$

$$RCH_2Li\ (RCH_2CH_2Li) + CH_2Br_2 \rightarrow RCH_2Br\ (RCH_2CH_2Br) + CH_2BrLi ,$$

$$RCH_2Li + RCH_2Br \rightarrow RCH_2CH_2R + LiBr .$$

Butyl-lithium reacts with bromochloromethane[31] at –110°C with formation of chloromethyl-lithium (90%) and bromochloromethyl-lithium (10%). The first compound was identified by carboxylation to chloroacetic acid. Its reaction with cyclohexene gives norcarane[32]. Chloromethyl-lithium is less stable than dichloromethyl-lithium.

Reactions of organolithium compounds with substituted dihalogenomethanes (dibromodiphenylmethane[33], 1,1-dibromoalkanes[30,34,35], and dichlorodiphenylmethane[29]) have been described. The products of the reaction of phenyl-lithium with dichlorodiphenylmethane are tetraphenylethylene and triphenylmethane.

Organolithium compounds react vigorously with tri- and tetra-halogenomethanes. The primary reaction product is a trihalogenomethyl derivative of lithium:

$$RLi + CXCl_3 \rightarrow RX + Cl_3CLi ,$$

$$(R{=}CH_3,\ C_2H_5,\ n\text{-}C_4H_9,\ C_6H_5\ \text{etc.},\ X{=}H,\ Cl,\ Br,\ I) .$$

† Here and henceforth the yield of the reaction product is indicated in brackets.

The formation of trichloromethyl-lithium has been demonstrated in the reaction of butyl-lithium with chloroform in tetrahydrofuran[39] or in a tetrahydrofuran–ethyl ether–petroleum ether mixture[11] at –110°C. The compound was identified by the products of its reaction with mercury(II) chloride, carbon dioxide, and benzophenone. The reaction with mercury(II) chloride led to the isolation of bis(trichloromethyl)mercury (m.p. 146.5–148.5°C with decomposition) in 91% yield. It has been noted[36] that trichloromethyl-lithium is less stable than dichloromethyl-lithium. At –65°C it decomposes in 30 min to the extent of 40–50%:

$$Cl_3CLi \rightarrow LiCl + \ddot{C}Cl_2 .$$

Tribromomethyl-lithium was obtained by the reaction[37] of butyl-lithium or phenyl-lithium with carbon tetrabromide in tetrahydrofuran solution at –110°C and also by the reaction[38] of trichloromethyl-lithium with carbon tetrabromide. It was identified by carboxylation to tribromoacetic acid. Bromoform is formed in its reaction with methanol[37].

Organolithium compounds react with $CXCl_3$ (X = H, Cl, Br, or I) in the presence of cyclohexene[11,25,26,36,39,40] with formation of 7,7-dichloronorcarane, the yield of which is 50–90%. However, the yield of 7,7-dibromonorcarane in the analogous reaction with bromoform[4,27] and carbon tetrabromide[26,37] is low (8–19%).

The formation of dihalogenonorcaranes has been regarded[33,36,41–43] as a result of the predominantly molecular interaction of trihalogenomethyl-lithium with the olefin and not the addition of the free dihalogenocarbene to cyclohexene.

Franzen[44–46] believes that butyl-lithium reacts with dibromodifluoromethane, forming free difluorocarbene. The latter adds to olefins, triphenylphosphine, and butyl-lithium taken in excess. The involvement of difluorocarbene is postulated in the reactions of the lithium compound with trifluoroiodomethane[47], which takes place with formation of tetrafluoroethylene (43%).

The reactions of organolithium compounds with polyhalogenomethanes are frequently employed as a source of carbenes for a wide variety of organic syntheses based on the latter.

Thus alkyl and aryl derivatives of lithium react vigorously with polyhalogenomethanes at a low temperature. In the initial stages of the reaction the corresponding halogenomethyl derivatives of lithium are produced. They decompose with formation of lithium halides and reactive carbenes.

It is to be expected that the organometallic compounds of the remaining alkali metals will react similarly with polyhalogenomethanes.

III. REACTIONS OF ORGANOMETALLIC COMPOUNDS OF GROUP II ELEMENTS

The reactions of organometallic compounds of Group II elements with polyhalogenomethanes have been investigated for magnesium, zinc, cadmium, and mercury compounds. In such reactions the organic derivatives of these elements show markedly different reactivities.

Organomagnesium compounds react vigorously with various halogeno-derivatives at low temperatures and therefore their reactions do not require initiation.

The alkyl compounds of zinc and cadmium react fairly readily with halogenomethanes ($CHBr_3$, $CHCl_3$, CCl_4) but the reactions of aryl derivatives take place only in the presence of an initiator.

The reactions of organomercury compounds with polyhalogenomethanes are observed on heating to the temperature of the onset of decomposition of the former compounds. The reactions occur more readily in the presence of oxygen and peroxides or under the influence of ultraviolet light.

1. Reactions of Organomagnesium, Organozinc, and Organocadmium Compounds

The reactions of organomagnesium compounds with polyhalogenomethanes have been investigated for asymmetric compounds of the type RMgX (R = alkyl, or aryl and X = halogen). The reaction of phenylmagnesium bromide[48] with chloroform leads to the formation of triphenylmethane (80%). Its yield is lower (about 25%) in the corresponding reactions[49] with bromoform and iodoform. Later it was shown[50] that chloroform reacts with phenylmagnesium bromide to form triphenylmethane (76%) and small amounts of biphenyl and bromobenzene. The products of the reaction of bromoform and iodoform with this magnesium derivative are tetraphenylethane (up to 60%) and triphenylmethane[51]. The products of the reaction of phenylmagnesium bromide with carbon tetrachloride are hexaphenylethane (50–80%) and bromobenzene[52]. A complex mixture of products is formed in the reactions of alkyl derivatives of magnesium. Ethylmagnesium bromide reacts with carbon tetrachloride to form methane and ethylene[53]. The products of its reaction with bromoform are ethyl bromide, methylene dibromide, 3-methylpentane, and acetylene[51].

The reactions of organomagnesium compounds have been investigated in greatest detail by Villieras[54–57]. It was established that these reactions, like those of organolithium compounds, lead to the formation of intermediate halogenomethyl derivatives of the metal. In the reaction of isopropylmagnesium chloride with dihalogenomethane[56] at −80°C the exchange of the halogen in CH_2X_2 for the MgCl group is observed, the halogens being arranged in the following sequence in terms of the ease of their exchange:

$$I > Br \gg Cl,$$
$$RMgCl + CH_2X_2 \rightarrow RX + XCH_2MgCl.$$

Grignard reagents react with bromotrichloromethane[56], carbon tetrachloride, and chloroform[57], forming the trichloromethyl derivative CCl_3MgX. The final products of the reaction of RCH_2MgCl with chloroform are RCH_2Cl and a mixture of olefins ($RCH{=}CHCH_2R$ and $RCH{=}CH_2$). In the reaction of organomagnesium compounds[57] with bromoform the products are alkyl bromides and the dibromomethyl compound $CHBr_2MgX$, which decomposes with formation of bromocarbene or reacts with the initial organometallic compound:

$$CHBr_2MgX + RMgX \rightarrow MgXBr + RCHBrMgX \downarrow \; RC\ddot{H} + MgXBr.$$

The alkylcarbene is converted into a mixture of various olefins. It is suggested[57] that the reactions of organomagnesium compounds with polyhalogenomethanes proceed via a four-centre transition state:

$$CHBr_3 + RMgCl \rightleftharpoons \left[\begin{matrix} HBr_2C\cdots MgCl \\ \quad\;\; \cdots \\ Br\cdots R \end{matrix}\right] \rightleftharpoons CHBr_2MgCl + RBr.$$

Organozinc and organocadmium compounds R_2M exhibit the same reactivity in relation to polyhalogenomethanes, which depends on the nature of the group R linked to the metal atom. Alkyl compounds of zinc[58–60] and cadmium[61] react vigorously with bromoform, chloroform, and carbon tetrachloride at room temperature. Diethylzinc also reacts with chloroiodomethane[62] and methylene di-iodide[63,64] with formation of unsaturated hydrocarbons. The reaction of diethylzinc with methylene di-iodide[65,66] and also with ethylidene di-iodide[67,68] in the presence of olefins is accompanied by the formation of cyclopropanes (30–90%):

$$(C_2H_5)_2Zn + CH_2I_2 \rightarrow C_2H_5I + C_2H_5ZnCH_2I \xrightarrow{>C=C<} >C(CH_3)-C< + C_2H_5ZnI.$$

Aryl compounds (diphenylzinc and diphenylcadmium[69]) do not react with chloroform and carbon tetrachloride even when the reaction mixture is heated to 100°C. However, in the presence of oxygen the reactions proceed readily at room temperature.

The principal products of the reaction of diethylcadmium with carbon tetrachloride are ethyl chloride, ethylcadmium chloride, and cadmium chloride, the yield of the latter increasing with the molar ratio[61] $OCl_4 : R_2Cd$. When cyclohexene is introduced into the reaction mixture, the reaction is retarded so much that an increase of temperature to 80°C is required for its occurrence. 7,7-Dichloronorcarane was not detected in the products. The mechanism of the reaction of diethylcadmium with carbon tetrachloride is somewhat obscure.

As mentioned above, aryl compounds of zinc and cadmium are inert with respect to polyhalogenomethanes under the usual conditions. When oxygen is introduced into the reaction mixture[70,71], the reaction between phenyl derivatives [of the two metals] and $CXCl_3$ (X = H or Cl) proceeds readily with formation of benzene (X = H), chlorobenzene (X = Cl), ααα-trichlorotoluene, phenol, biphenyl, and hexachloroethane. The initiating effect of oxygen is associated with the oxidation of the organometallic compound, which is accompanied by the generation of phenyl radicals. The latter react with the polyhalogenomethane or the initial zinc or cadmium compound:

$$C_6H_5^{\cdot} + CXCl_3 \rightarrow C_6H_5X + Cl_2C^{\cdot},$$
$$(X{=}H, D, Cl)$$
$$C_6H_5^{\cdot}\,(Cl_2C^{\cdot}) + (C_6H_5)_2M \rightarrow C_6H_5C_6H_5\,(C_6H_5CCl_3) + C_6H_5M^{\cdot},$$
$$(M{=}Zn, Cd)$$
$$C_6H_5M^{\cdot} + CXCl_3 \rightarrow C_6H_5MCl + \dot{C}XCl_2,$$
$$2\dot{C}XCl_2 \rightarrow CXCl_2{-}CXCl_2.$$

Thus the reaction of diphenylzinc[71] and diphenylcadmium[70] with chloroform and carbon tetrachloride in an oxygen atmosphere involves the participation of free radicals.

2. Reactions of Organomercury Compounds

The greatest number of communications deal with reactions of organomercury compounds with chloroform and carbon tetrachloride. Mercury compounds react with polyhalogenomethanes on heating to the temperatures of the onset of decomposition of the organometallic compound. As early as 1864, Alexeyeff and Beilstein concluded[60] that the reaction of diethylmercury with bromoform is accompanied by the formation of ethyl bromide and propene. In the reaction of diethylmercury with iodoform[72], ethylmercury iodide, ethyl iodide, ethylene, and acetylene are formed. Diphenylmercury does not react at 130°C with bromoform and chloroform but does react with iodoform, forming tri-iodomethylphenylmercury[73] $C_6H_5HgCI_3$ (m.p. 153–155°C). We believe that the asymmetric mercury

compound and the corresponding halogenomethyl derivatives of magnesium discussed above are not formed by the same mechanism. In the present case the reaction probably begins with the decomposition of iodoform:

$$CHI_3 \rightarrow HI + \ddot{C}I_2 ,$$
$$(C_6H_5)_2Hg + HI \rightarrow C_6H_6 + C_6H_5HgI ,$$
$$C_6H_5HgI + \ddot{C}I_2 \rightarrow C_6H_5HgCI_3 ,$$
$$C_6H_5HgCI_3 + \ddot{C}I_2 \rightarrow C_6H_5HgI + C_2I_4 .$$

These processes account for the formation of the reaction products.

Diphenylmercury and dinaphthylmercury[74-76] begin to react with chloroform and carbon tetrachloride above 200°C. The principal products of the reaction of diphenylmercury with the above halogenomethanes are phenylmercury chloride, benzene, $\alpha\alpha\alpha$-trichlorotoluene, and hexachloroethane. The reaction has a free-radical mechanism:

$$R_2Hg \rightarrow RHg^{\cdot} + R^{\cdot} , \quad (1)$$
$$RHg^{\cdot} + CXCl_3 \rightarrow RHgCl + Cl_2XC^{\cdot} , \quad (2)$$
$$(X=H, Cl)$$
$$R^{\cdot} + CXCl_3 \rightarrow RX + Cl_3C^{\cdot} ,$$
$$Cl_3C^{\cdot} + R_2Hg \rightarrow RCCl_3 + RHg^{\cdot} , \quad (3)$$
$$2Cl_3C^{\cdot} \rightarrow C_2Cl_6 .$$

Phenylmercury radicals not only react with the polyhalogenomethane to form phenylmercury chloride but also decompose with the liberation of mercury or recombine:

$$2RHg^{\cdot} \rightarrow RHg{-}HgR \rightarrow R_2Hg + Hg .$$

Alkyl compounds of mercury[77-79] R_2Hg (R = C_2H_5,[79] n-C_3H_7,[78,80] iso-C_3H_7,[77] and n-C_4H_9[79]) react in a more complex manner with chloroform and carbon tetrachloride, forming alkylmercury chloride, mercury, calomel, alkyl chloride, chloroform, saturated hydrocarbons (RH) and olefins (R-H), and hexachloroethane, and in the reaction with chloroform also methylene dichloride. The initial stage of these reactions is the dissociation of the organometallic compound into radicals according to Eqn. (1). Possibly there is a molecular interaction of the organomercury compound with the polyhalogenomethane accompanied by the formation of alkyl mercury chloride and free radicals:

$$R_2Hg + CXCl_3 \rightleftarrows [R_2Hg \cdot Cl_3XC] \rightarrow RHgCl + R^{\cdot} + Cl_2XC^{\cdot} . \quad (4)$$

One can also postulate that in the initial reaction stage a trichloromethyl derivative of mercury is formed and serves as a source of dichlorocarbene, which would initiate the process. However, the introduction into the reaction mixture of trichloromethyl compounds of mercury[79], which decompose under the reaction conditions with generation of $\ddot{C}Cl_2$, did not lead to its acceleration.

The occurrence of free-radical processes has been confirmed using inhibitors[79]. It has been shown[77-79] that initiated decomposition of the initial organometallic compound plays a considerable role in these reactions:

$$R^{\cdot} (Cl_2XC^{\cdot}) + RHgR \rightarrow RH (Cl_2XCH) + \dot{R}_{-H}HgR . \quad (5)$$

This results in the formation of unstable organomercury radicals with an unpaired electron at the carbon atom. The nature of their decomposition depends to a considerable degree on the nature of the alkyl group linked to the metal atom:

$$\dot{R}_{-H}HgR \begin{cases} \rightarrow R_{-H} + RHg^{\cdot} , & (a) \\ \rightarrow R_{-H} + Hg + R^{\cdot} . & (b) \end{cases} \quad (6)$$

The radicals formed from the ethyl derivative decompose both via mechanism (6a) and (6b). With increase of the chain length of the primary alkyl residue (R = n-C_3H_7 and n-C_4H_9), their decomposition takes place predominantly via reaction (6b), while the corresponding derivative containing a secondary alkyl residue (iso-C_3H_7 and s-C_4H_9) is cleaved with formation of alkylmercury radicals via reaction (6a). The latter react with chloroform and carbon tetrachloride forming the alkyl mercury chloride [reaction (2)].

Alkyl radicals participating in the reaction initiate the decomposition of the organometallic compound or react with polyhalogenomethanes. It has been shown for isopropyl radicals[77] that they abstract from chloroform not only hydrogen atoms but also chlorine atoms. The ease of abstraction of hydrogen, deuterium, and chlorine from $CHCl_3$ and $CDCl_3$ decreases in the sequence H > Cl ≃ D.

Among organomercury compounds, alkoxy-derivatives[80,81] of the type RHgOR′ react with chloroform most readily. Their reaction[81] takes place at room temperature with a quantitative yield of the corresponding trichloromethyl compounds:

$$RHgOR' + CHCl_3 \rightarrow RHgCCl_3 + R'OH$$
$$(R=n\text{-}C_3H_7, \text{ cyclo-}C_6H_{11}, C_6H_5CH_2, C_6H_5; R'=(CH_3)_3C) .$$

Thus the thermal reactions of the symmetrical mercury compounds R_2Hg with polyhalogenomethanes have a free-radical mechanism.

Organomercury compounds dissociate into radicals under the influence of ultraviolet light:

$$R_2Hg{-} \begin{cases} \rightarrow 2R^{\cdot} + Hg , \\ \rightarrow RHg^{\cdot} + R^{\cdot} . \end{cases}$$

The photochemical reaction of mercury compounds with polyhalogenomethanes takes place readily at room temperature. These processes were investigated in greatest detail by Razuvaev and coworkers.

The photolysis of R_2Hg has been investigated in solution in bromoform (R = C_6H_5,[82] carboxyphenyl, or methoxycarbonylphenyl[83]), chloroform (R = CH_3,[84] C_2H_5,[85] 2-methoxycarbonylethyl[86], mesityl[87], $C_6H_5CH_2$,[88] $C_6H_5CH_2CH_2$,[89] C_6H_5,[82,90] o-tolyl[91], p-tolyl[92], p-anisyl[93], p-chlorophenyl[91], carboxyphenyl and methoxycarbonylphenyl[83], α-naphthyl[94], and β-naphthyl[95]) and carbon tetrachloride (R = CH_3,[84,96] C_2H_5,[79] n-C_3H_7,[78,79] iso-C_3H_7,[78,79] n-C_4H_9,[79] s-C_4H_9,[79] $C_6H_5CH_2$,[96] C_6H_5,[75,90,96] o-tolyl[91], p-tolyl[92], p-anisyl[93], carboxyphenyl and methoxycarbonylphenyl[83], α-naphthyl[94], and β-naphthyl[95]). In these reactions the RHg radicals abstract a halogen atom from the polyhalogenomethane. Mercury and calomel are formed together with the alkyl- or aryl-mercury chloride. The yields of these substances depend on the nature of the group R linked to the mercury atom. The relative amounts of mercury and alkylmercury chloride vary particularly markedly in the photochemical reactions of alkyl derivatives of mercury with carbon tetrachloride. As in thermal reactions, the yield of mercury increases with the chain length of the primary alkyl residue[79] (more than 90% for di-n-propylmercury). On the other hand, with the secondary isopropyl residue, the corresponding alkylmercury chloride is formed preferentially. In these processes the organomercury compounds undergo initiated decomposition via mechanisms (5) and (6). In contrast to thermal reactions, the olefins formed react with the solvent giving 1,1,1-trichloroalkanes or 1,1,1,3-tetrachloroalkanes:

$$-\overset{|}{C}=\overset{|}{C}- + Cl_3C^{\cdot} \rightarrow -\overset{|}{\dot{C}}-\overset{|}{C}CCl_3 \xrightarrow{CXCl_3} -\overset{|}{C}X-\overset{|}{C}CCl_3 \quad (7)$$
$$(X = H, Cl)$$

The presence of calomel in the reaction mixture is due to the reaction of mercury[97] with carbon tetrachloride or the dealkylation of alkylmercury chloride under the influence of radicals:

$$RHgCl + Cl_3C^{\cdot} \rightarrow CHCl_3 + \dot{R}_{-H}HgCl \rightarrow R_{-H} + {}^1/_2Hg_2Cl_2 . \quad (8)$$

The radical R formed in the reaction interacts with the organometallic compound or the halogeno-derivative, abstracting chlorine from carbon tetrachloride or hydrogen from chloroform and bromoform, with the exception of benzyl radicals[88] which largely recombine. In the photolysis of organomercury compounds in a mixture of a protic solvent (alcohol, ethylcellosolve) and carbon tetrachloride the R radicals react only with the first solvent, abstracting a hydrogen atom[98] and forming RH.

In the photochemical reactions with chloroform and carbon tetrachloride the asymmetric organometallic compounds RHgR′ also undergo dealkylation[88,98,99] with formation of RHgCl. The more firmly bound group remains attached to mercury. In many cases the process is accompanied by symmetrisation[100]:

$$2RHgR' \rightarrow R_2Hg + R'_2Hg .$$

Among the mixed mercury compounds, peroxy-derivatives of the type[101] RHgOOR′, hydroxides[102-106] RHgOH (R = C_6H_5,[102,103,105,106] $C_6H_5CH_2$,[103] mesityl[104], or *p*-dimethylaminophenyl[104]), and benzyl- and phenylmercury derivatives of succinimide[107,108] react most readily with carbon tetrachloride and chloroform. The reactions of these compounds lead to the formation of the corresponding chlorides RHgCl.

In the case of many hydroxides, the initial stage of the process is usually believed to be their dissociation into radicals:

$$RHgOH \rightarrow RHg^{\cdot} + HO^{\cdot} .$$

We believe that the mechanism of the reaction of the hydroxides with polyhalogenomethanes is more complex. It is doubtful if these compounds undergo homolysis at the Hg–O bond, which is stronger than the Hg–C bond. Probably the comparatively ready occurrence of the reaction is due to the participation in it of oxides, which are present in the hydroxides and are formed as a result of the dehydration of the latter[109]:

$$2RHgOH \rightleftarrows (RHg)_2O + H_2O .$$

This conclusion is based on the finding that alkoxy-derivatives of mercury RHgOR′ (in this case R′ = RHg) react with polyhalogenomethanes under fairly mild conditions.

The reactions of organomercury compounds with halogenomethanes do not take place solely under the influence of heat and light. Organic peroxides and oxygen have an initiating effect on them. Razuvaev showed[74] that the temperature in the reaction of diphenylmercury with carbon tetrachloride may be considerably reduced (from 260° to 50°C) when benzoyl peroxide is introduced into the reaction mixture. Acetyl peroxide has a similar effect[110]. The principal reaction products are phenylmercury chloride, ααα-trichlorotoluene, and hexachloroethane. In the reaction with chloroform the products are benzene, phenylmercury chloride, and also small amounts of ααα-trichlorotoluene and hexachloroethane. The initial stage of the process is the decomposition of the acyl peroxide:

$$(R'COO)_2 \rightarrow R'^{\cdot} + R'COO^{\cdot} + CO_2 ,$$
$$(R' = CH_3, C_6H_5)$$

The methyl or phenyl radicals formed in this process interact with carbon tetrachloride generating trichloromethane radicals. ααα-Trichlorotoluene is formed via reaction (3) and phenylmercury chloride via reaction (2). The reaction of asymmetric organometallic compounds RHgR′ with carbon tetrachloride in the presence of peroxides[111,112] is similar to that of diphenylmercury. It has been established that the affinity for the free radical $Cl_3C^{\cdot}$ decreases in the series 2,4,6-$(CH_3)_3C_6H_2$, α-$C_{10}H_7$, *p*-$CH_3C_6H_4$, *o*-$CH_3C_6H_4$, *m*-$CH_3C_6H_4$, C_6H_5, C_2H_5, C_4H_9, $C_6H_5CH_2$, cyclo-C_6H_{11}.

The more reactive group R in RHgR′ recombines with the trichloromethyl radical and the group R′ remains bound to mercury in the resulting compound R′HgCl.

Alkyl derivatives of mercury react somewhat differently with carbon tetrachloride in the presence of a peroxide. The principal products of the reaction of dibutylmercury[113] with carbon tetrachloride (100°C, 7h) initiated by benzoyl peroxide are 1,1,1,3-tetrachloropentane, butyl chloride, chloroform, mercury, and butylmercury chloride. 1,1,1-Trichloropentane was not detected. On the basis of the reaction products, it was concluded that trichloromethyl radicals react with the organometallic compound, forming chloroform:

$$Cl_3C^{\cdot} + R_2Hg \rightarrow R_{-H} + CHCl_3 + RHg^{\cdot} .$$
(olefin)

It is believed[113] that butylmercury radicals decompose with liberation of mercury (up to 63–73%) or react with carbon tetrachloride, forming butylmercury chloride. The formation of tetrachloropentane is due to reaction (7). Under the influence of radicals, dibutylmercury undergoes a decomposition in this reaction analogous to that described above for the thermal and photochemical reactions of alkyl compounds of mercury[79] [reactions (5) and (6)].

Perbenzoic acid[114], the peroxides formed by the oxidation of benzaldehyde or cyclohexene[115], t-butyl peroxide[116], t-butyl hydroperoxide[116], and oxygen[79] have an initiating effect on the reaction of diphenylmercury with carbon tetrachloride or chloroform. It is suggested that perbenzoic acid initially reacts with the organometallic compound to form phenylmercury perbenzoate[114], which decomposes into radicals. t-Butyl hydroperoxide reacts similarly[116]:

$$R_2Hg + (CH_3)_3COOH \rightarrow RH + RHgOOC(CH_3)_3 \begin{cases} \rightarrow RHg^{\cdot} + (CH_3)_3COO^{\cdot}, \\ \rightarrow RHgO^{\cdot} + (CH_3)_3CO^{\cdot} . \end{cases}$$

The initiating effect of t-butyl peroxide[78,116] is due to its reaction with the organometallic compound induced by the nucleophilic attack by active oxygen on the mercury atom with formation of a complex. The decomposition of the latter is accompanied by the generation of free radicals:

$$R_2Hg + (CH_3)_3COOC(CH_3)_3 \rightleftarrows \left[\begin{matrix} R\text{—}Hg\text{—}R \\ \uparrow \\ (CH_3)_3COOC(CH_3)_3 \end{matrix} \right] \rightarrow \begin{matrix} RHgOC(CH_3)_3 \\ + \\ R^{\cdot} + (CH_3)_3CO^{\cdot} \end{matrix}$$

(R = n-C_3H_7,[78] iso-C_3H_7,[78] or C_6H_5[116]).

In these reactions alkyl derivatives of mercury and the alkylmercury chlorides formed mainly decompose under the influence of radicals[78] [see reactions (5), (6), and (8)]. The olefins thus produced react with the solvent, giving a high yield of the corresponding trichloro- or tetrachloroalkanes [reaction (7)].

Organometallic compounds of the type R_2Hg (R = C_2H_5,[79] n-C_3H_7,[78] iso-C_3H_7,[117,118] n-C_4H_9,[79] s-C_4H_9,[79] t-C_4H_9,[118] cyclo-C_6H_{11},[119] or C_6H_5[79]) react comparatively readily with carbon tetrachloride or chloroform in the presence of oxygen. The initial step in the reaction is nucleophilic attack by oxygen on the mercury atom in the

organometallic compound accompanied by the formation of an unstable organomercury peroxide[118,120,121]:

$$R_2Hg + O_2 \rightleftarrows [R_2Hg^{\cdot}O_2] \rightarrow RHgOOR \begin{cases} \longrightarrow RHg^{\cdot} + RO_2^{\cdot}, \\ \longrightarrow RHgO^{\cdot} + RO^{\cdot}. \end{cases}$$

The oxidation products of an organomercury compound[118,120,121] are an alkoxy-compound RHgOR, an alcohol ROH, a ketone or an aldehyde, mercury, and also hydrocarbons. The oxidation is accompanied by the generation of free radicals which react with polyhalogenomethanes. The alkoxy-compound obtained also readily reacts with chloroform and carbon tetrachloride. This results in the formation of a trichloromethyl compound of mercury, which decomposes under the reaction conditions into an alkylmercury chloride and dichlorocarbene:

$$RHgCCl_3 \rightleftarrows RHgCl + \ddot{C}Cl_2 . \qquad (9)$$

In the reactions with added cyclohexene in the reaction mixture, 7,7-dichloronorcarane was detected[79]. Seyferth et al. established[122] that reaction (9) is reversible and the rate of decomposition depends on the nature of the solvent.

The oxidation of organomercury compounds in solution in polyhalogenomethanes is accompanied by initiated decomposition processes via mechanisms (5), (6), and (8), which in this case are less important than in thermal and photochemical reactions in the absence of oxygen[79]. Regardless of the nature of the alkyl group, the main dealkylation product of the organometallic compound is alkylmercury chloride.

Diphenylmercury is known to react[123] with chloroform in the presence of bismuth trichloride, forming phenylmercury chloride, benzene, and biphenyl. Bismuth trichloride probably behaves as a catalyst.

Thus organomercury compounds of the type R_2Hg do not react with polyhalogenomethanes under ordinary conditions. Their reaction is observed only under the influence of heat, ultraviolet light, oxygen, or organic peroxides and proceeds via a free-radical mechanism.

IV. REACTIONS OF ORGANIC COMPOUNDS OF GROUP III ELEMENTS

The reactions of organometallic compounds of group III elements with polyhalogenomethanes have been investigated mainly for alkyl compounds of aluminium and thallium. There is only one report[124] of the reaction of triethylindium-ether with chloroform and bromoform in hexane solution accompanied by the formation of the corresponding diethylindium halide. The reactions of organoboron compounds with polyhalogenomethanes have been described using as examples the reactions of vinylarylboron butoxide with bromotrichloromethane[125] at room temperature under the influence of ultraviolet light:

$$CH_2{=}CH{-}\underset{\displaystyle C_6H_5}{\underset{|}{B}}{-}OC_4H_9 + CBrCl_3 \rightarrow Cl_3CCH_2CHBr{-}\underset{\displaystyle C_6H_5}{\underset{|}{B}}{-}OC_4H_9 .$$

The first report on the reaction of organoaluminium compounds with chloroform and carbon tetrachloride was published by Hilpert and Grüttner[126]. In particular, they concluded that, when triphenylaluminium is dissolved in chloroform, triphenylmethane and a crystalline substance, probably diphenylaluminium chloride, are formed. The views concerning the reactivity of alkyl compounds of aluminium in relation to polyhalogenomethanes and the mechanism of their reaction with the latter are extremely contradictory.

It has been noted[127] that triethylaluminium reacts slowly with methylene dichloride at 55°C. Under these conditions, ethylaluminium sesquichloride and diethylaluminium hydride do not react with this chloro-derivative. However, methylene di-iodide reacts with triethylaluminium[128] (in molar proportions of 1 : 2) in benzene solution at room temperature with formation of ethyl iodide and ethylene. The iodomethyl derivative of diethylaluminium is formed as an intermediate:

$$R_3Al + CH_2I_2 \rightarrow RI + R_2AlCH_2I \rightarrow R_2AlI + {}^1/_2C_2H_4 .$$

When the reaction was carried out with added cyclohexene, norcarane was isolated (20%). The participation of free carbene in the reaction has not been suggested[129,130].

Chloroform reacts with triethylaluminium[127,131] more vigorously than does methylene dichloride. For equimolar proportions of the reactants, the main products are methylene dichloride and ethyl chloride. At 70°C hydrocarbons (butane, butene, hexane, and hexene) are formed in addition to the above compounds. The reaction of diethylaluminium hydride with chloroform (at the boiling point of the latter) is accompanied by the formation of methyl chloride. Under these conditions, ethylaluminium sesquichloride does not react with trichloromethane. The reaction of aluminium compounds with chloroform is regarded as a free-radical process[127]. However, Miller[128] believes that the reactions of organoaluminium compounds with trihalogenomethanes proceed via a stage involving the formation of halogenomethyl derivatives. In particular, he showed that triethylaluminium reacts with bromoform in benzene solution, forming the dibromomethyl derivative $(C_2H_5)_2AlCHBr_2$.

There are contradictory data on the behaviour of organoaluminium compounds in carbon tetrachloride solutions. According to some reports[132,133], a mixture of such compounds explodes. According to others[134,135], aluminium compounds do not react with carbon tetrachloride at room temperature and the latter is recommended as a solvent for them. Vigorous reaction between triethylaluminium and carbon tetrachloride with evolution of gaseous substances is observed in the presence of titanium tetrachloride[135]. It is suggested that diethylaluminium dichloride is formed initially and is then readily dealkylated[136] by carbon tetrachloride. It is believed[135] that the reaction proceeds with participation of a carbonium ion:

$$2CCl_4 + C_2H_5AlCl_2 \rightleftarrows 2Cl_3C^{\cdot} + C_2H_5^{+}AlCl_4^{-},$$

$$C_2H_5^{+}AlCl_4^{-} + CCl_4 \rightarrow C_2H_5Cl + CCl_3^{+}AlCl_4^{-} \rightarrow AlCl_3 + CCl_4 ,$$

$$C_2H_5^{+}AlCl_4^{-} + C_2H_5AlCl_2 \rightarrow C_2H_6 + (AlCl_4^{-} + \overset{+}{C}_2H_4AlCl_2) \downarrow 2\,AlCl_3 + C_2H_4 .$$

In contrast to ethylaluminium dichloride, diethylaluminium chloride does not react with carbon tetrachloride in boiling benzene[137].

Reinheckel[127,138,139] elucidated the reactions of organoaluminium compounds with carbon tetrachloride to the greatest extent. He showed that, depending on the reaction conditions (molar ratio of the starting materials and temperature of the reaction mixture), the type of interaction changes. A 1 : 3 mixture of triethylaminium and carbon tetrachloride is safe at 0°C, but explodes at 20°C. The mixture in molar proportions of 1 : 10 can be controlled not only at room temperature but also at 75–80°C. The main reaction products are chloroform, methylene chloride, and monochloro-substituted methane, ethane, and propane. These compounds are also formed in the reaction of ethylaluminium dichloride[139] with carbon tetrachloride. Diethylaluminium and carbon tetrachloride in

proportions of 1 : 5 react slowly with formation of chloroform and ethyl chloride. A mixture of diethylaluminium hydride and carbon tetrachloride in molar proportions of 1 : 3 explodes at 80°C, but when the reaction ratio is changed to 1 : 5 the reaction takes place smoothly. The sesquichloride reacts with carbon tetrachloride at a moderate rate in proportions of 1 : 10 but an equimolar mixture explodes at room temperature[127]. Reinheckel believes that these reactions have a free-radical mechanism. At the same time it has been shown[140] that tri-isobutylaluminium reacts with carbon tetrachloride, forming a trichloromethyl derivative:

$$R_3Al + CCl_4 \rightarrow RCl + R_2AlCCl_3 \rightarrow R_2AlCl + \ddot{C}Cl_2 .$$

The yield of di-isobutylaluminium chloride is 92% and that of isobutyl chloride 25%. The dichlorocarbene formed reacts with the initial organometallic compound or cyclohexene and gives rise to 7,7-dichloronorcarane in reactions where the olefin has been added.

The literature data discussed above lead to the conclusion that the initial stage in the reaction of organoaluminium compounds with polyhalogenomethanes, as for the lithium and magnesium compounds, is the formation of the corresponding intermediate halogenomethyl derivatives, which decompose with generation of carbenes. By virtue of their exothermic nature, these reactions are probably accompanied by the thermal decomposition of the organoaluminium compounds.

It has been suggested[141] that unstable halogenomethyl derivatives are formed in the reaction of trimethylthallium with polyhalogenomethanes: CHX_3 (X = Cl, Br, or I) and methylene dichloride and dibromide. The reaction products are methane and $(CH_3)_2TlX$. However, trimethylthallium does not react with carbon tetrachloride and methylene dichloride at room temperature. The reaction of dimethylthallium ethoxide with chloroform results in a quantitative yield of dimethylthallium chloride[141].

V. REACTIONS OF ORGANIC COMPOUNDS OF GROUP IV ELEMENTS

The majority of organic derivatives of non-transition elements (silicon, germanium, tin, and lead) react with polyhalogenomethanes in the same way as organomercury compounds, in the presence of initiators or catalysts. The reactivity increases from silicon to lead compounds. Organotitanium compounds, which have covalent Ti–C σ bonds, react with halogenomethanes much more readily.

1. Reactions of Organosilicon and Organogermanium Compounds

Organosilicon and organogermanium derivatives are fairly inert in relation to polyhalogenomethanes. Tetraphenylsilicon[142] does not react with carbon tetrachloride at the boiling point of the reaction mixture. Tributylgermanium hydride[143–145] reacts with carbon tetrachloride only at 200–220°C with formation of tributylgermanium chloride and chloroform.

The unusual behaviour of tetraethylsilicon in carbon tetrachloride solution on irradiation with ultraviolet light is of interest. Under these conditions, tetraethylsilicon is chlorinated without the abstraction of a radical with formation of chloroethyltriethylsilicon[146] (tetraphenylsilicon and methyltriphenylsilicon did not undergo any changes). The reactions of organosilicon compounds of the type R_4Si, R_3SiH, and R_6Si_2 with polyhalogenomethanes under the influence of organic peroxides have been described.

The main products of the reaction of tetraethylsilicon[146] with carbon tetrachloride in the presence of acyl peroxides are, as in the photochemical reaction, chloroethyltriethylsilicon (a mixture of α- and β-isomers) and chloroform. The free radicals formed in the decomposition of the initiator react with tetraethylsilicon:

$$R'^{\cdot} + (C_2H_5)_4Si \rightarrow R'H + (C_2H_5)_3Si\dot{C}_2H_4 , \quad (10)$$

$$(C_2H_5)_3Si\dot{C}_2H_4 + CCl_4 \rightarrow (C_2H_5)_3SiC_2H_4Cl + Cl_3C^{\cdot} , \quad (11)$$

$$Cl_3C^{\cdot} + (C_2H_5)_4Si \rightarrow CHCl_3 + (C_2H_5)_3Si\dot{C}_2H_4 .$$

In the presence of benzoyl peroxide organosilicon compounds containing double bonds[147] combine with $CXCl_3$ (X = H or Cl) via a free-radical mechanism:

$$R_3SiCH{=}CH_2 \xrightarrow{CXCl_3} R_3SiCHX - \dot{C}H_2CCl_3 . \quad (12)$$

A reaction analogous to reaction (12) has also been described for unsaturated organogermanium compounds[148]. Acetylene derivatives of silicon react with bromotrichloromethane and dibromodichloromethane on irradiation of the reaction mixture by ultraviolet light with formation of the corresponding bromochloropropenylsilanes[149,150].

The reaction of substituted silanes with $CXCl_3$ (X = H, Cl, or Br), carbon tetrabromide, and methylene dibromide has been investigated in the presence of benzoyl peroxide[151–157], t-butyl peroxide[154], and also catalysts—palladium[158], iron pentacarbonyl, or chloroplatinic acid[159]. In this process the polyhalogenomethane is reduced: CX_4 to CHX_3, CHX_3 to CH_2X_2, etc. In the presence of peroxycompounds the reactions proceed via a free-radical chain mechanism[151–157]:

$$(C_6H_5COO)_2 \rightarrow 2C_6H_5COO^{\cdot} ,$$

$$C_6H_5COO^{\cdot} + R_3SiH \rightarrow C_6H_5COOH + R_3Si^{\cdot} ,$$

$$R_3Si^{\cdot} + CH_nX_{4-n} \rightarrow R_3SiX + \dot{C}H_nX_{3-n} ,$$

$$(n=1, 2;\ X=Cl, Br)$$

$$\dot{C}H_nX_{3-n} + R_3SiH \rightarrow CH_{n+1}X_{3-n} + R_3Si^{\cdot} .$$

It has been shown by ESR[160] that the photochemical reaction of substituted silanes and also germanes and stamanes with carbon tetrachloride in the presence of t-butyl peroxide is accompanied by the formation of trichloromethyl radicals:

$$(CH_3)_3COOC(CH_3)_3 \xrightarrow{h\nu} 2(CH_3)_3CO^{\cdot} ,$$

$$(CH_3)_3CO^{\cdot} + R_3EH \rightarrow (CH_3)_3COH + R_3E^{\cdot} ,$$

$$(E=Si, Ge, Sn)$$

$$R_3E^{\cdot} + CCl_4 \rightarrow R_3ECl + Cl_3C^{\cdot} .$$

Photolysis of triethylsilicon iodide in methylene dichloride, chloroform, or carbon tetrachloride solution leads to the formation of triethylsilicon chloride[161]. Polyhalogenomethanes can be arranged in the following sequence in terms of the ease of exchange of iodine for chlorine:

$$CCl_4 > CHCl_3 > CH_2Cl_2 .$$

It is suggested that this exchange takes place via a free-radical chain mechanism.

The reaction of diphenylsilane with methylene di-iodide in the presence of olefins[162] at 189°C is accompanied by the formation of cyclopropanes (17–38%).

The reaction of hexamethyldisilane[163] with carbon tetrachloride in the presence of benzoyl peroxide (at 80°C) or t-butyl peroxide (at 129°C) takes place without the dissociation of the Si–Si bond. It is suggested that (pentamethyldisilyl)methyl radicals participate in the reaction:

they recombine or abstract a chlorine atom from carbon tetrachloride. The primary process is the decomposition of the initiator into radicals, which then react with the initial silicon compound:

$$R^{\cdot} + (CH_3)_6Si_2 \rightarrow R'H + (CH_2)_5Si_2\dot{C}H_2,$$
$$2\,(CH_3)_5Si_2\dot{C}H_2 \rightarrow (CH_3)_5Si_2CH_2CH_2Si_2(CH_3)_5,$$
$$(CH_3)_5Si_2\dot{C}H_2 + CCl_4 \rightarrow (CH_3)_5Si_2CH_2Cl + Cl_3C^{\cdot},$$
$$Cl_3C^{\cdot} + (CH_3)_6Si_2 \rightarrow CHCl_3 + (CH_3)_5Si_2\dot{C}H_2.$$

2. Reactions of Organotin and Organolead Compounds

Organotin and organolead compounds have almost the same reactivity with respect to polyhalogenomethanes. The chemical reactivity of these compounds depends on their type. The hydrides R_3MH react most readily, compounds of the type R_6M_2 react with more difficulty, and the reaction involving R_4M (M = Sn or Pb) is more difficult still. The tetra-aryl organometallic compounds[142] do not react with carbon tetrachloride at the boiling point of the reaction mixture. Tetra-alkyl compounds of tin[164] also do not react with carbon tetrachloride at 100°C. In contrast to the alkoxy-compounds of mercury, monoalkoxy-derivatives of tin are inert with respect to chloroform. Trimethyltin t-butoxide did not react with chloroform on heating the reaction mixture at 140°C for 1 h.[81] However, amino-compounds of the type $R_3SnNR'_2$ undergo an exothermic reaction with CHX_3 (X = Cl or Br), forming trihalogenomethyl derivatives of the organometallic compounds[165-167]:

$$R_3SnNR'_2 + CHX_3 \rightarrow R_3SnCX_3 + R'_2NH.$$

When a mixture of tetra-alkyl compounds of tin with trifluoroiodomethane is heated, fluoroform is formed. In the reaction of tetramethyl-lead with the above halogeno-derivative, a methyl group of the organometallic compound is exchanged for a trifluoromethyl group[168,169], which results in the formation of trifluoromethyltrimethyl-lead $(CH_3)_3PbCF_3$. The reaction takes place similarly under the influence of ultraviolet light. It is suggested that the trifluoromethyl derivative of lead is formed by a free-radical mechanism.

The photochemical reactions of organotin compounds of the type R_4Sn (R = CH_3,[170,171] C_2H_5,[171] n-C_3H_7,[170,171] or C_6H_5[172]) with carbon tetrachloride[171,172] and chloroform[170-172] have been investigated in greater detail. The monochloride and dichloride of alkyl- or aryl-tin derivatives, hydrocarbons, and hexachloroethane were isolated as the main products. In the reaction of the alkylated organometallic compounds with carbon tetrachloride, chloroform and 1,1,1,3-tetrachloroalkanes [see reaction (7)] are also formed. The first step in the reaction is photolysis of the organometallic compound to R and R_3Sn radicals or of carbon tetrachloride to Cl and Cl_3C radicals. Trialkyl(aryl)stannyl radicals react with chloroform or carbon tetrachloride. The resulting $CXCl_2$ radicals (X = H or Cl) react with the alkylated organometallic compounds:

$$\dot{C}XCl_2 + R_4Sn \rightarrow CHXCl_2 + R_3Sn\dot{R}_{-H} \rightarrow R_3Sn^{\cdot} + \underset{\text{(olefin)}}{R_{-H}}.$$

In contrast to the corresponding silicon derivatives [reactions (10) and (11)], the organotin radicals with an unpaired electron at the carbon atom decompose and split off an olefin. Under the reaction conditions, the monochloride of trialkyl(aryl)tin also interacts with polyhalogenomethanes forming R_2SnCl_2.

It is interesting to note that the photolysis of asymmetric tin compounds containing alkyl and aryl groups is accompanied by the abstraction of aryl radicals. Following the reaction of diethyldiphenyltin and dibenzyldiphenyltin[173] with carbon tetrachloride and chloroform, the dichloride of the corresponding dialkyltin was isolated from the reaction mixture.

The photochemical reactions of organolead compounds with polyhalogenomethanes have been hardly investigated. It has been noted[172] that tetraphenyl-lead reacts with chloroform and carbon tetrachloride similarly to diphenylmercury. Diphenyl-lead dichloride, lead chloride, benzene or chlorobenzene, hexachloroethane, and, in the case of chloroform, also metallic lead were isolated from the reaction mixture.

The photolysis of triphenyltin and triphenyl-lead azides in methylene dichloride solution[174] is accompanied by the generation of $(C_6H_5)_3M$ radicals, which react with the halogenomethane, forming triphenyltin or triphenyl-lead chlorides (51-75%).

Oxygen and organic peroxides initiate the reactions of organotin and organolead compounds. The alkyl derivatives of tin[164] R_4Sn (R = C_2H_5, n-C_3H_7, or iso-C_3H_7) react in an atmosphere of oxygen with carbon tetrachloride at 100°C, forming trialkyltin, chloroform, and 1,1,1,3-tetrachloroalkanes as the main products. The organotin compound with a secondary alkyl group (tetraisopropyltin) reacts with carbon tetrachloride at a lower temperature (60°C). It has been noted[175] that oxygen greatly accelerates the reaction of tetramethyl-lead with carbon tetrachloride, which is accompanied by the formation of a white precipitate. The initiating effect of oxygen is associated with the formation of free radicals in the oxidation of the initial tin and lead compounds[176].

The reactions of many organotin compounds (tetraethyltin[177], diethyldimethyltin[177], tetraphenyltin[178], and triethyltin chloride[177]) with carbon tetrachloride in the presence of benzoyl peroxide have been investigated. The reaction of tetraethyltin with carbon tetrachloride at 75-90°C yields triethyltin chloride, diethyltin dichloride, chloroform, ethylene, ethane, benzoic acid, carbon dioxide, and many other compounds[177]. Under these conditions, triethyltin chloride reacts with carbon tetrachloride similarly to tetraethyltin, forming the same products. Tetraphenyltin undergoes complete dearylation. Tin(IV) chloride, chlorobenzene, hexachloroethane and benzoic and phthalic acids were isolated from the reaction mixture[178]. Tetraphenyl-lead reacts with carbon tetrachloride in the presence of benzoyl peroxide, forming diphenyl-lead dichloride and dibenzoate[178]. These reactions are initiated by the free radicals formed as a result of the decomposition of benzoyl peroxide. The above processes have free-radical chain mechanisms.

Organotin compounds with an unsaturated alkyl group (triethylvinyltin[179] and triphenylvinyltin[180]) combine with polyhalogenomethanes $CXCl_3$ [X = H, Cl, or Br; see the analogous reaction (12)] in the presence of benzoyl peroxide.

The reactions of tin and lead compounds with carbon tetrachloride in the presence of catalysts have been described. In the presence of bismuth trichloride (0.5-1.0 mole per mole of the organometallic compound) the tetraphenyl compounds react with carbon tetrachloride at the boiling point of the reaction mixture, forming chlorobenzene, triphenyltin chloride or triphenyl-lead chloride, and diphenyl-lead dichloride. Bismuth trichloride was recovered quantitatively from the reaction mixture[142]. Alkyl[181,182] and aryl[183,184] compounds of tin also undergo

dealkylation (dearylation) at a comparatively low temperature in the presence of bismuth and aluminium chlorides in chloroform solution.

In the presence of aluminium chloride or boron trifluoride tetramethyl- and tetraethyl-lead[185] react with methylene dibromide, forming compounds having the composition $R_3PbCH_2PbR_3$.

As the number of alkyl (aryl) groups linked to the metal atom decreases, the reactivity of the organotin and organolead compounds in relation to polyhalogenomethanes rises. In contrast to the tetra-alkyl derivatives, hexacyclohexyldilead reacts with carbon tetrachloride even at room temperature, forming tricyclohexyl-lead chloride and dicyclohexyl-lead dichloride[175]. Possibly a trichloromethyl derivative of lead is formed as an intermediate in this process:

$$(C_6H_{11})_3PbPb(C_6H_{11})_3 + CCl_4 \rightarrow (C_6H_{11})_3PbCl + (C_6H_{11})_3PbCCl_3 .$$

In the presence of oxygen the reaction terminates much faster. Then the main products are the chlorides of tricyclohexyl-lead and dicyclohexyl-lead (in nearly equimolar proportions), cyclohexyl chloride, hexachloroethane, and carbon dioxide. In an atmosphere of oxygen this organometallic compound reacts vigorously with carbon tetrabromide and is quantitatively converted into dicyclohexyllead dibromide. The problem of the involvement of trihalogenomethyl compounds in these reactions remains unresolved. However, the analogous trihalogenomethyl derivative of tin has been isolated from the reaction mixture in the reaction between hexamethylditin and trifluoroiodomethane. The reaction takes place on heating[186] to 80°C or on irradiation with ultraviolet light[187,188]:

$$(CH_3)_3SnSn(CH_3)_3 + CF_3I \rightarrow (CH_3)_3SnI + (CH_3)_3SnCF_3 .$$

It is suggested that trifluoromethyltrimethyltin is formed in these processes by a free-radical mechanism:

$$R_3SnSnR_3 \rightarrow 2R_3Sn^{\cdot} ,$$
$$R_3Sn^{\cdot} + CF_3I \rightarrow R_3SnCF_3 + I^{\cdot} ,$$
$$I^{\cdot} + R_3SnSnR_3 \rightarrow R_3SnI + R_3Sn^{\cdot} .$$

One cannot exclude the possibility of the formation of an intermediate complex of the organometallic compound with trifluoroiodomethane.

The reactions of hexa-alkylditin compounds with carbon tetrachloride are initiated by oxygen and acyl peroxides[177,189]. In an atmosphere of oxygen, hexaethylditin reacts with carbon tetrachloride forming a mixture of triethyltin and diethyltin chloride[177]. The products of the reaction carried out in the presence of benzoyl peroxide are ethane, ethylene, butane, carbon dioxide, chloroform, triethyltin chloride and benzoate, and diethyltin dichloride[177,189]. These processes have a free-radical mechanism. The high yields of chloroform and ethylene indicate the abstraction of hydrogen atoms from the ethyl group of the organometallic compound by trichloromethyl radicals:

$$Cl_3C^{\cdot} + (C_2H_5)_6Sn_2 \rightarrow CHCl_3 + (C_2H_5)_5Sn_2\dot{C}_2H_4$$
$$\downarrow$$
$$(C_2H_5)_3Sn^{\cdot} + C_2H_4 + (C_2H_5)_3Sn ,$$
$$(C_2H_5)_3Sn^{\cdot} + CCl_4 \rightarrow (C_2H_5)_3SnCl + Cl_3C^{\cdot} ,$$
$$(C_2H_5)_2Sn \xrightarrow{CCl_4} (C_2H_5)_2SnCl_2 .$$

In the presence of freshly precipitated copper, hexaalkylditin compounds react with carbon tetrachloride under milder conditions[190]. Hexaethylditin and hexabutylditin react with carbon tetrachloride at room temperature, forming trialkyltin chloride, chloroform, hexachloroethane, copper chlorides, and coloured organotin compounds.

The reactions of organotin hydrides R_3SnH with polyhalogenomethanes proceed in the absence of initiators or catalysts. The reaction of triphenyltin hydride[145,191] with carbon tetrachloride is exothermic. This results in quantitative yields of chloroform and triphenyltin chloride. Triphenyltin hydride reacts less vigorously with chloroform and methylene dichloride[176]. The reaction leads to the reduction of chloroform to methylene dichloride and of the latter to methyl chloride. Polyhalogenomethanes can be arranged in the following sequence in terms of the rates of the above reactions:

$$CCl_4 > CHCl_3 > CH_2Cl_2 .$$

Alkyltin hydrides also reduce polyhalogenomethanes[192-194]. Tributyltin hydride reduces carbon tetrachloride to chloroform (about 85%) and the latter to methylene dichloride[192]. The above organometallic compound reacts with bromoform and tribromofluoromethane[192], forming tributyltin bromide (up to 95%) and methylene dibromide (62%) and dibromofluoromethane (69%) respectively.

The chemical reactivity of the hydrides depends on the nature of the alkyl group. The rate of reaction of tributyltin hydride with carbon tetrachloride and chloroform is appreciably lower than that of trimethyltin hydride[193].

Owing to their low thermal stability, organolead hydrides have been little investigated. They are much more reactive than the corresponding tin hydrides. The reaction of trialkyltin hydrides with carbon tetrachloride involves the reduction of the latter to chloroform[195].

The mechanism of the reaction of organolead and organotin hydrides with polyhalogenomethanes is insufficiently clear. It is believed that these reactions have a free-radical mechanism.

3. Reactions of Organotitanium Compounds

Among the organometallic compounds of Group IV elements, titanium derivatives have been most thoroughly investigated. In the present review we shall discuss the reactions with polyhalogenomethanes of compounds where an organic group is bound covalently to the titanium atom, i.e. compounds with metal–carbon σ bonds.

The reactions of di- and tetra-valent titanium derivatives with chloroform and carbon tetrachloride were investigated in greatest detail by Razuvaev and coworkers. Titanium(II) derivatives (diphenyltitanium and cyclopentadienylphenyltitanium) are thermally stable. Their reactions with chloroform and carbon tetrachloride involve the splitting off of phenyl groups and the oxidation of titanium to the tetravalent state[196,197]. The products of the reaction of diphenyltitanium[196] with chloroform at room temperature are titanium tetrachloride, benzene, and biphenyl. Cyclopentadienyltitanium trichloride ($C_5H_5TiCl_3$) is formed in the reactions of cyclopentadienylphenyltitanium[197]. Probably the primary step in the reaction is the formation of a complex of the organometallic compound and the polyhalogenomethane, the subsequent reaction of which involves the generation of phenyl radicals.

Compounds of tetravalent titanium of the type R_nTiX_{4-n} ($n = 1, 2, 3$, or 4) have been investigated in greatest detail. They are less stable than the organic derivatives of divalent titanium.

The reaction of tetramethyl titanium[198] with gaseous trifluoroiodomethane in 2 : 1 ethyl ether–hexane solution at −78°C results in the formation of trimethyltitanium iodide and methyl iodide. Tetramethyltitanium-ether

reacts with carbon tetrachloride, forming methyl chloride, methane, and titanium tetrachloride[199]. The products of the reaction of tetramethyl titanium with carbon tetrachloride in ethereal solution in the presence of mercury indicate a homolytic mechanism of this reaction[200]:

$$(CH_3)_4Ti + 2CCl_4 + Hg \rightarrow 3CH_4 + CH_3HgCl + TiCl_4 + Cl_3C^{\cdot}.$$

This is confirmed also by the fact that the analogous system tetraphenyl-lithium–carbon tetrachloride initiates the low-temperature free-radical polymerisation of vinyl chloride[201].

Cyclopentadienyltriphenyltitanium reacts with chloroform between −70° and −50°C. This results in an almost quantitative yield of benzene and cyclopentadienyltitanium trichloride[202].

The reactions of dicyclopentadienyldimethyltitanium[203] and dicyclopentadienyldiphenyltitanium[204,205] with carbon tetrachloride at 60–80°C are accompanied by the dissociation of σ bonds and the retention of the sandwich group. The products are dicyclopentadienyltitanium dichloride (about 75%), hexachloroethane, and respectively methyl chloride (95%) and chlorobenzene. In the thermal reaction of chloroform with $(C_5H_5)_2Ti(CH_3)_2$, dicyclopentadienyltitanium dichloride (75%) and methane (80%) are also formed. Dibenzyldicyclopentadienyltitanium reacts with chloroform similarly[203]. The thermal and photochemical reactions of $(C_5H_5)_2Ti(C_6H_5)_2$ with chloroform are accompanied by the formation of $(C_5H_5)_2TiCl_2$ and benzene[204–206]. It is suggested that dicyclopentadienyltitanium is an intermediate in these reactions:

$$(C_5H_5)_2TiR_2 \rightarrow (C_5H_5)_2Ti + 2R^{\cdot},$$
$$R^{\cdot} + CXCl_3 \rightarrow RX + Cl_3C^{\cdot},$$
$$(X = H, Cl)$$
$$(C_5H_5)_2Ti \xrightarrow{CXCl_3} (C_5H_5)_2TiCl_2.$$

The reactions of organotitanium compounds of this type with polyhalogenomethanes are initiated by oxygen[204,205]. The reaction of dicyclopentadienyldiphenyltitanium with carbon tetrachloride takes place in the presence of oxygen at a lower temperature (45–55°C). Then phosgene, biphenyl, and small amounts of phenol are formed together with dicyclopentadienyltitanium dichloride and chlorobenzene.

Reactions of titanium compounds of the type $RTiCl_3$ (R = CH_3 or C_6H_5) with carbon tetrachloride and chloroform have been described. Phenyltitanium trichloride reacts with chloroform, forming benzene and biphenyl. Chlorobenzene was not detected in the reaction with carbon tetrachloride[207]. The reaction of methyltitanium trichloride[208–210] with carbon tetrachloride leads to the formation of methyl chloride. Data indicating a free-radical mechanism of these reactions have been adduced[209].

VI. REACTIONS OF TWO-ELEMENT ORGANIC COMPOUNDS

The chemistry of organic compounds with two and more non-organic elements, i.e. the chemistry of compounds with carbon–element–element bonds, is developing vigorously at the present time. The previous section dealt with reactions of two-element organic compounds of the type R_3E-ER_3 (E = Si, Sn, or Pb) with polyhalogenomethanes. It is useful to discuss also reactions of organic derivatives having bonds between two different elements. It should only be noted that, despite the large variety of compounds of this type which have been obtained, their reactivity in relation to polyhalogenomethanes has been scarcely investigated. There are only a few data on the reactions of the compounds R_3EM (E = Si, Ge, Sn, or Pb and M = Li or Na) with alkyl halides.

The reactions of triphenylsilyl-lithium with polyhalogenomethanes have been investigated in greater detail. The reaction of this compound with methylene dichloride[211–213] results in the formation of hexaphenyldisilane, methyltriphenylsilane, chloromethyltriphenylsilane, and bis(triphenylsilyl)methane in proportions which depend on the reaction conditions. It is suggested[213] that chloromethyl derivatives of lithium, which serve as a source of carbenes, are formed in these reactions. Their mechanism may be represented as follows:

$$R_3SiLi + CH_2Cl_2 \rightarrow R_3SiCl + CH_2ClLi \rightarrow \ddot{C}H_2 + LiCl,$$
$$R_3SiCl + R_3SiLi \rightarrow R_3SiSiR_3 + LiCl,$$
$$R_3SiLi + \ddot{C}H_2 \rightarrow R_3SiCH_2Li,$$
$$R_3SiCH_2Li \xrightarrow{CH_2Cl_2} R_3SiCH_2Cl + CH_2ClLi,$$
$$R_3SiCH_2Li \xrightarrow{R_3SiCl} R_3SiCH_2SiR_3 + LiCl,$$
$$R_3SiCH_2Li \xrightarrow{H_2O} R_3SiCH_3.$$

Methylene di-iodide reacts similarly. The reaction of triphenylsilyl-lithium with methylene dibromide leads to the formation of hexaphenyldisilane (42–60% with respect to Ph_3SiLi), methyltriphenylsilane (up to 40%), and bromomethyltriphenylsilane (about 10%) with respect to methylene dibromide).

The products of the reaction of triphenylsilyl-lithium[212,213] with CHX_3 (X = Cl, Br, and I) are methyltriphenylsilane, hexaphenyldisilane, mono- and di-halogenomethyltriphenylsilanes, bis(triphenylsilyl)methane, and triphenylsilane. Probably the initial stage is the following process:

$$R_3SiLi + CHX_3 \rightarrow R_3SiH + CX_3Li \rightarrow \ddot{C}X_2 + LiX,$$
$$R_3SiLi + CHX_3 \rightarrow R_3SiX + CHX_2Li \rightarrow \ddot{C}HX + LiX.$$

It has been shown that the yield of reaction products depends on the reactant ratio. In the reaction between the organometallic compound and methyl iodide in molar proportions of 3 : 1, hexaphenyldisilane (60.5% with respect to Ph_3SiLi), bis(triphenylsilyl)methane (19.5%), and methyltriphenylsilane (24% with respect to iodoform) are formed. A change in reactant ratio to 2 : 1 leads to the formation of hexaphenyldisilane and almost equimolar amounts of monoiodomethyl- and di-iodomethyl-triphenylsilanes.

Hexaphenyldisilane (56–73%) and dichloromethyltriphenylsilane (11–42%) are formed at −60°C in the reaction of triphenylsilyl-lithium[213] with carbon tetrachloride. The reaction with carbon tetrabromide is much more complex.

The reactions of triphenylgermylsodium[214–216] with methylene dichloride, chloroform, and carbon tetrachloride have been carried out in liquid ammonia and in ether. The main product of the reaction with methylene dichloride is bis(triphenylgermyl)methane. The above organometallic compound reacts with chloroform and carbon tetrachloride in ethereal solution in a more complex manner, forming mainly hexaphenyldigermane[215,216].

It is interesting to note that bis(triethylgermyl)cadmium[217], like the organometallic alkyl derivatives R_2Cd, reacts vigorously with carbon tetrachloride. The reaction mixture explodes at room temperature. Triethylgermanium chloride (41%), dichlorobis(triethylgermyl)methane (55%), and cadmium chloride (91.5%) are formed in the reaction carried out at −75°C. The mechanism of the reaction has not been elucidated. It is suggested that

dichlorocarbene is involved in the reaction. Probably derivatives of the type $R_3GeCdCCl_3$ or R_3GeCCl_3 are produced as intermediates.

The corresponding mercury compound (like R_2Hg) proved to be less reactive with respect to carbon tetrachloride. The photochemical reaction[218] of bis(triethylgermyl)mercury with carbon tetrachloride involves the formation of mercury (60%), triethylgermanium chloride (36%), and hexachloroethane.

Tris(trimethylsilyl)thallium reacts with chloroform, forming bis(trimethylsilyl)thallium chloride, but does not react with methylene dichloride[219].

The reaction of tris(trimethylsilyl)silane with carbon tetrachloride leads to the formation of tris(trimethylsilyl)silicon chloride and chloroform[220]:

$$[(CH_3)_3Si]_3SiH + CCl_4 \xrightarrow{\text{reflux.}} [(CH_3)_3Si]_3SiCl + CHCl_3 .$$

The reactions of trialkyl(aryl)stannylsodium with methylene dichloride[221,222], chloroform[223-225], and carbon tetrachloride[222,223] have been investigated. The reaction with methylene dichloride results in the formation of the corresponding bis[trialkyl(aryl)stannyl]methanes. The reaction with chloroform is more complex. Trimethylstannylsodium and triphenylstannylsodium react with carbon tetrachloride, forming hexamethyl- and hexaphenylditin.

The reaction of triphenylplumbyl-lithium with methylene dichloride, chloroform, and carbon tetrachloride in tetrahydrofuran solution at −60°C leads to the formation of a high yield of the corresponding bis-, tris-, and tetrakis-(triphenylplumbyl)methanes[226]. The reactions with bromochloromethane yield[227,228] a mixture of compounds, the main component of which is a derivative of the type $R_3Pb(CH_2)_nPbR_3$.

Prolonged photolysis (100 h) of the complex compounds lithium or potassium tetraphenylborates in chloroform solution is accompanied by the formation of benzene, biphenyl, triphenylboron and respectively lithium or potassium chlorides[229]. It is suggested[230] that these reactions take place with participation of phenyl radicals.

The above review shows that organic derivatives with two "non-organic" elements react with polyhalogenomethanes in a fairly complex manner. The mechanism of these processes is still not entirely clear.

VII. REACTIONS OF ORGANIC COMPOUNDS OF GROUP V ELEMENTS

The reactions of organic compounds of phosphorus, arsenic, antimony, and bismuth with polyhalogenomethanes have been described for derivatives of the type R_3E and R_5E. The first data on the reactivity of organophosphorus compounds with respect to polychloromethanes[231-233] were obtained in studies on the chemical properties of triethylphosphine. In particular it was stated that this compound forms an adduct with carbon tetrachloride having the composition $3(C_2H_5)_3P.CCl_4$.

Organic derivatives of tervalent elements combine with trichloroiodomethane[234], forming an adduct with the composition $R_3E.CCl_3I$. The reactions were carried out in ether with the reaction mixture cooled to −46°C. The following compounds were obtained in this way (the melting points and decomposition temperatures are indicated in brackets): $(CH_3)_3P.CCl_3I$ (10°C, decomposes), $(C_6H_5)_3P.CCl_3I$ (72°C, 110°C), $(CH_3)_3As.CCl_3I$ (39°C, 95°C), $(C_6H_5)_3As.CCl_3I$ (−30°C, 100°C), and $(CH_3)_3Sb.CCl_3I$ (5°C, 82°C).

Triphenylantimony in ether does not react with trichloroiodomethane at temperatures ranging from −78° to 20°C. Nor does it react with chloroform when the reaction mixture is illuminated. However, photolysis of triphenylbismuth in chloroform solutions is accompanied by the formation of bismuth trichloride, bismuth, and benzene. Bismuth trichloride and biphenyl are formed in the photochemical reaction with carbon tetrachloride[172].

It has been noted[234] that trimethylphosphine does not react with carbon tetrachloride. However, later it was shown[235] that trialkylphosphines react with carbon tetrachloride in ether when the temperature of the reaction mixture is −10°C. The formation of phosphonium compounds is suggested:

$$R_3P + CCl_4 \rightarrow R_3P\langle^{CCl_3}_{Cl} \qquad (R = n\text{-}C_4H_9,\ n\text{-}C_5H_{11} \text{ etc.}) .$$

In the presence of methanol the latter form trialkylphosphine oxides, methyl chloride, and chloroform:

$$R_3P\langle^{CCl_3}_{Cl} + CH_3OH \rightarrow R_3PO + CH_3Cl + CHCl_3 .$$

Similar results were obtained somewhat earlier[236] in the reaction of triphenylphosphine with carbon tetrachloride or bromotrichloromethane in the presence of ethanol. The mechanism of the reactions of triphenylphosphine with carbon tetrachloride and carbon tetrabromide has been discussed[237-239]. It is believed that a phosphonium compound, formed as a result of the nucleophilic attack by phosphorus on the halogen, is an intermediate in the reaction:

$$R_3\ddot{P}\langle^{X}_{CX_3} \rightarrow R_3P^{+}\langle^{X^-}_{CX_3} \rightarrow R_3P\langle^{X}_{CX_3} , \quad (X = Cl^{237,238}, Br^{239}) \qquad (13)$$

$$R_3P\langle^{X}_{CX_3} + R_3P \rightarrow R_3P{=}CX_2 + R_3PX_2 .$$

The presence of dihalogenomethylenetriphenylphosphorane was established on the basis of the products of the reaction with carbonyl compounds, in particular with benzaldehyde[237,239]:

$$R_3P{=}CX_2 + C_6H_5CHO \rightarrow R_3PO + C_6H_5CH{=}CX_2 .$$

Triphenylphosphine[236] does not react with chloroform and bromoform on heating the reaction mixture to 80°C, but does react with bromoform in the presence of benzoyl peroxide[240]. The initiating effect of the latter was not confirmed in a subsequent investigation[236]. Triphenylphosphine reacts with bromoform at 150°C, forming dibromomethyltriphenylphosphonium bromide[236]:

$$R_3P + CHBr_3 \rightarrow [R_3PCHBr_2]^+Br^- .$$

The reactions of alkyl esters of alkyl- or aryl-phosphinous acids with carbon tetrachloride have been investigated[235,241]. The aryl derivatives[241] react according to the mechanism

$$Ar_2POR + CCl_4 \rightarrow Ar_2P(O)CCl_3 + RCl ,$$
$$(R = C_2H_5,\ n\text{-}C_3H_7) .$$

Reactions of compounds of the type $(RO)_3P$ with polyhalogenomethanes are not considered in this review.

The reaction of amino-substituted alkylphosphines with carbon tetrachloride results in the formation of 1,1,1-trichloroalkanes[242]. Trichlorobutane was isolated in 50% yield from the reaction mixture of bis(diethylamino)propylphosphine with carbon tetrachloride.

The reactions of organic derivatives of the elements of the type R_5E with polyhalogenomethanes have been investigated for pentaphenylphosphorane and pentaphenylantimony. Pentaphenylphosphorane reacts with chloroform and carbon tetrachloride at room temperature. Wittig and Geissler[243] reported that the reaction of this compound with chloroform has an ionic mechanism and involves the formation of tetraphenylphosphonium chloride and benzylidene chloride. In a more detailed study of the reaction of pentaphenylphosphorane with chloroform and carbon tetrachloride by Razuvaev and coworkers[244-248], it was established that these processes take place with participation of free radicals. This results in the formation of a quantitative yield of tetraphenylphosphonium chloride and of chlorobenzene (64%) in the reaction with carbon tetrachloride and of benzene (60–65%) in the reaction with chloroform. Benzylidene dichloride was not detected.

Pentaphenylantimony reacts similarly with chloroform and carbon tetrachloride[249]. Tetraphenylantimony chloride, biphenyl, and respectively benzene or chlorobenzene are formed in thermal reactions (100°C, 20–25 h) and in photolysis. The mechanism of these processes may be represented as follows:

$$R_5E \rightarrow R_4E^{\cdot} + R^{\cdot},$$
$$(E=P, Sb)$$
$$R_4E^{\cdot} + CXCl_3 \rightarrow R_4ECl + \dot{C}XCl_2,$$
$$(X=H, Cl)$$
$$R^{\cdot} + CXCl_3 \rightarrow RX + Cl_3C^{\cdot},$$
$$2R'' \rightarrow R'-R'.$$
$$(R'=Cl_3C, CXCl_2, R)$$

The photolysis of t-butylperoxytetraphenylantimony in carbon tetrachloride and chloroform solutions was investigated recently[250]. The reaction with carbon tetrachloride involves predominantly the dissociation of the Sb–O bond and the formation of tetraphenylantimony chloride (up to 83%). In the reaction with chloroform tetraphenylantimony chloride (41%), tetraphenylantimony oxide (40%), t-butyl alcohol (44%), and benzene (17%) were obtained, together with phenol (6%) and acetone (10%) as side products. These compounds are formed owing to the dissociation of the Sb–O and O–O bonds in the initial compound.

Thus the mechanism of the reaction of organic derivatives of the elements of the type R_3E with polyhalogenomethanes differs radically from the mechanism of the corresponding reactions with compounds of the pentavalent elements R_5E.

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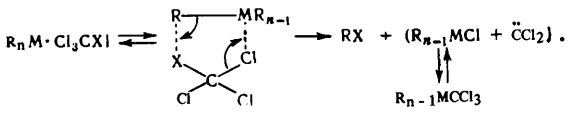
Organic derivatives of the elements can be divided into two groups in terms of their reactivity with respect to polyhalogenomethanes. The first includes organic compounds of alkali and evidently alkaline earth metals and Group III metals and also the alkyl compounds of zinc and cadmium, derivatives of divalent tin, and true organometallic derivatives of transition metals (in particular divalent titanium compounds). Their reactions with alkyl halides do not require initiation. Probably the primary step in the reaction of these organometallic compounds with polyhalogenomethanes is nucleophilic attack by the halogen on the metal accompanied by the formation of a complex and then of the corresponding halogenomethyl organometallic derivatives:

$$R_nM + CXCl_3 \rightleftarrows [R_nM \cdot Cl_3CX] \rightarrow R_{n-1}MCCl_3 + RX.$$
$$(X=H, Cl, Br, I)$$

One cannot exclude the possibility that the compound reacts via a five-membered cyclic transition state with formation of the corresponding carbene and its subsequent insertion into the metal–halogen bond formed:



The insertion of carbenes into the metal–halogen bond is used as one of the methods for synthesising halogenomethyl organometallic compounds. Possibly the reaction of the halogenomethyl complex formed with certain organometallic compounds (in all probability with divalent titanium compounds) is associated with the generation of free radicals.

It is striking that the reactions of the majority of organometallic compounds of this group with polyhalogenomethanes are exothermic. Owing to the lack of kinetic data, the mechanism of these reactions still remains insufficiently elucidated.

The addition of polyhalogenomethanes of the type CYX_3 (Y = H, Cl, Br, or I; X = Cl or Br) to compounds of tervalent Group V elements R_3E (E = P, As, or Sb) evidently takes place as a result of nucleophilic attack by the element on the halogen [reaction (13)], which leads to the formation of the corresponding halogenomethyl derivatives.

The second group includes the aryl derivatives of zinc and cadmium, organic compounds of mercury (R_2Hg), titanium, tin, and lead of the type R_4M, compounds of silicon and germanium, and compounds of pentavalent phosphorus, arsenic, antimony, and bismuth. These compounds are less reactive. Their reactions with polyhalogenomethanes takes place on heating, irradiation with light, or in the presence of initiators, and clearly have a distinct free-radical mechanism.

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Kinetics and Mechanism of the Reaction of Peroxy-compounds with Phosphites, Sulphides, and Aromatic Amines

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The studies dealing with the elucidation of the detailed mechanism and quantitative kinetics of the reactions of peroxy-compounds with phosphites, sulphides, and aromatic amines are reviewed. It is shown how evidence has been obtained by ESR of the existence of the one-electron amine oxidation stage, i.e. the stage involving the formation of radical-cations. The consecutive reactions of the radical-cations formed initially and their relation to the behaviour of the amines as polymerisation initiators are analysed. The characteristics of the detection of free radicals in reactions of phosphites and sulphides with hydroperoxides are examined and certain criteria of the latent radical nature of these reactions are formulated. In the last section correlations of the Hammett equation type for rates of the reactions under consideration and also the correlation between the rate constants on the one hand and the ionisation potentials and electron affinities on the other are discussed within the framework of the one-electron oxidation-reduction mechanism. The bibliography includes 96 references.

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I. INTRODUCTION

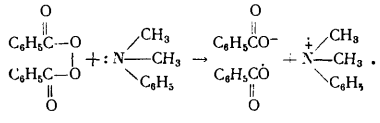
The reduction of peroxy-compounds by phosphites, sulphides, and aromatic amines constitutes a large and important class of organic reactions. On the basis of N. M. Semenov's hypothesis concerning the possibility of the formation of free radicals in the bimolecular interaction between valence-saturated molecules, one may also expect the formation of radicals in the above reactions. This assumption follows from the fact that, since one of the reactants (the peroxide) is a powerful oxidising agent and the other is a powerful reducing agent, the reaction does not require a large activation energy (10–20 kcal mole^{-1}). However, one cannot exclude the possibility that another mechanism, which does not lead to the formation of free radicals, is even more effective. There is no unanimous view in the literature concerning the mechanism of the reactions of peroxy-compounds with amines, phosphites, and sulphides; therefore, it is necessary to make a critical analysis of the results available in this field and their interpretation.

Moreover, there is also a purely practical aspect of the investigation of these reactions associated with the behaviour of aromatic amines as initiators of the radical polymerisation of monomers, phosphites, and sulphides and as synergists in polymer stabilisation processes.

II. KINETICS AND MECHANISM OF REACTIONS OF AROMATIC AMINES

The chemistry of the interaction of aromatic amines with peroxy-compounds, particularly with benzoyl peroxide[1-6], has been investigated in greatest detail. Gambaryan[1] established that primary, secondary, and tertiary aromatic amines rapidly react with benzoyl peroxide (BP) with formation of benzoic acid and *O*-benzoylhydroxylamine or its *N*-alkyl derivatives.

According to Horner's hypthesis[2,3], the first stage for all amines is the formation of a complex of the amine and benzoyl peroxide in which an electron is transferred from the lone pair of the amine to the peroxide molecule, involving the formation of an ion pair and a benzoate radical. For example, for dimethylaniline (DMA) (a tertiary amine), we have



The second stage consists in proton transfer from the methyl group or the benzene ring of the amine radical-cation to the benzoate anion; this is accompanied by the formation of a radical pair, which enters into further reactions leading to the formation of the final products. The appearance of an intense colour when dimethylaniline reacts with benzoyl peroxide in chloroform in the presence of chloride ions is regarded by Horner and Schwenk[2] as evidence of the formation of the dimethylaniline radical-cation.

Dimethylaniline radicals were first obtained by the irradiation of the initial amines with light[7] at a wavelength of 2700 Å or by flash photolysis[8] and were investigated spectophotometrically[7,8]. The absorption spectrum of the radical-cations in aqueous and EPA (ether : isopentane : ethanol = 5 : 5 : 2) solutions is characterised by a broad band with a maximum at 4600 Å.

The appearance of a band with a more diffuse maximum at 4600–4700 Å was observed by Stavrova et al.[9] in the reaction between benzoyl peroxide and dimethylaniline in EPA at 20°C; they attributed this band to the dimethylaniline radical-cation formed as a primary species. Indeed, this result is without any doubt evidence of the formation of amine radical-cations in the benzoyl peroxide–dimethylaniline system. However, the problem arises whether these radical-cations are primary or secondary species. Spectrophotometry cannot provide an unambiguous and reliable answer; electron spin resonance (ESR) is likely to be the most suitable method.

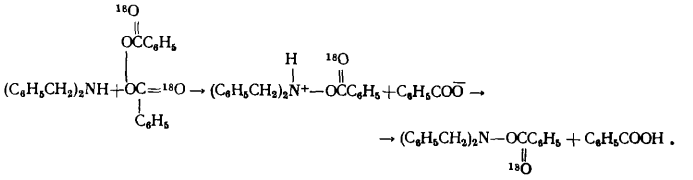
The formation of neutral free radicals in the reaction of benzoyl peroxide with dimethylaniline and other tertiary amines was observed directly in a number of studies. Horner[2] showed that the benzoyl peroxide–dimethylaniline system is capable of initiating the radical polymerisation of various vinyl compounds at 20°C, the initiating agent being the benzoate radical. An analogous initiation effect in the polymerisation of styrene was also observed following the addition of *p*-dimethyltoluidine to benzoyl peroxide[10]. Imoto et al.[11] determined the effectiveness of the initiation at 25°C of the polymerisation of styrene by the benzoyl peroxide–dimethylaniline system. They compared the rate of initiation calculated from the rate of polymerisation and the values of $k_p/k_t^{1/2}$ with the rates of reaction of benzoyl peroxide and dimethylaniline; the effectiveness of the initiation proved to be 0.25. Hrabák[5,12] showed that the rate of reaction of dimethylaniline, methyltolyltoluidine, and tritolylamine with benzoyl peroxide in benzene solution decreased severalfold in the presence of the stable diphenylpicrylhydrazyl (DPPH) radicals or nitric oxide; the replacement of benzene by other solvents also led to retardation of the reaction. The results can be explained by the fact that the radicals arising in the bimolecular reaction of benzoyl peroxide with tertiary amines (HA) initiate the chain reaction according to the mechanism

$$C_6H_5COO\dot{} + HA \rightarrow C_6H_5COOH + \dot{A}\,, \qquad (1)$$

$$\dot{A} + (C_6H_5COO)_2 \rightarrow C_6H_5COO^{\cdot} + C_6H_5COOA\,. \qquad (2)$$

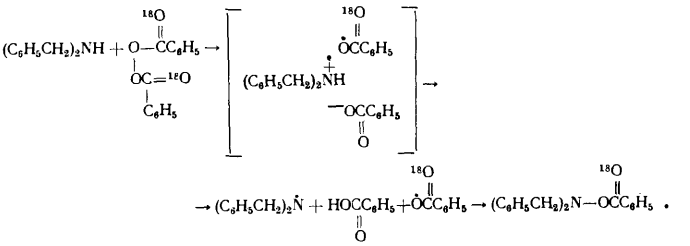
The kinetics of the reaction of benzoyl peroxide with dimethylaniline were studied by many investigators[6,10-15], all of whom established that the rate is proportional to the concentration of amine and peroxide in accordance with a bimolecular mechanism of the initial stage of the process. In one of the papers[6] the activation energy for this reaction is quoted as 14.8 kcal mole^{-1}; according to another[17], it is 12.8 kcal mole^{-1}. As regards the initiation of polymerisation as a method for the quantitative determination of radicals, the studies on different monomers[14-17] yielded for the rate of polymerisation w_n a relation of the type $w_n = k[DMA]^{1/2}[BP]^{1/2}$ corresponding to a bimolecular formation of benzoate radicals. Since the reaction between benzoyl peroxide and dimethylaniline is of the chain type, the experimentally observed second order can be accounted for only by cross termination by benzoate and amine (A) radicals.

Donald and Dorothy Denny[18] investigated the mechanism of the reaction of secondary amines with benzoyl peroxide using isotope tracers. Thus, when benzoyl peroxide, the carbonyl oxygen of which contained 1.32 at.% ^{18}O, was allowed to react with dibenzylamine, *O*-benzoyl-*NN*-dibenzylhydroxylamine was isolated in 57% yield as the product. Chemical determination of ^{18}O showed that the same amount of the isotope is retained in the carbonyl groups of both *O*-benzoyl-*NN*-dibenzylhydroxylamine itself and the product of its solvolysis by sodium ethoxide—(ethyl benzoate). On the basis of these results, a mechanism was proposed, as an alternative to that of Horner, involving a nucleophilic attack by the amine on the peroxy-bond with formation of an ion pair, which is converted into the reaction products via proton transfer:



A similar mechanism is suggested also for the reactions of primary amines[18].

It is noteworthy that the distribution of oxygen-18 in the reaction products may be explained within the framework of the one-electron transfer hypothesis:



Moreover, many facts are contrary to the concept of a nucleophilic mechanism. For example, secondary and primary amines initiate at 25°C the polymerisation of monomers[20,21], although with a low effectiveness; thus the effectiveness for diphenylamine (DPA) [20] is about 10^{-3}. The absorption of nitric oxide by the reacting benzoyl peroxide–diphenylamine system[22] indicates the intermediate formation of free radicals. Bagdasar'yan and Milyutinskaya[20] showed that these radicals are capable of reacting with diphenylpicrylhydrazine (DPPH-H), which is then oxidised to DPPH radicals. Finally, free radicals were detected[23] by ESR following the mixing of benzene solutions of benzoyl peroxide and aniline or its *p*-methyl and *p*-ethyl derivatives (at 20°C); in all cases these proved to be diphenyl(diaryl)nitroxide radicals.

The hyperfine coupling (HFC) constants for the ^{14}N nuclei and the protons of the aromatic ring and the g-factors for these radicals (2.0059) agree well with the above interpretation of the ESR spectra.

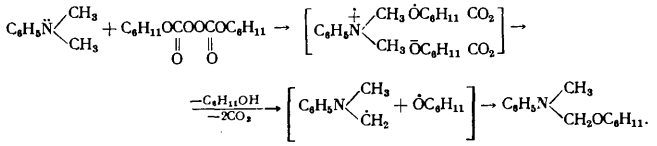
However, direct evidence of the formation of radical-cations derived from the secondary or primary amines (according to Horner's mechanism) is not given in any of the studies quoted above; moreover, all the facts confirming the radical mechanism of the reaction of these amines with benzoyl peroxide are frequently associated with secondary radical products.

The reaction of benzoyl peroxide with aniline, diphenylamine, and secondary aliphatic amines is of the second order (according to the initial rates) and has low activation energies: 16.4 kcal mole^{-1} for diphenylamine[20], 10.7 kcal mole^{-1} for aniline[20], 10.5 kcal mole^{-1} for diethylamine[22], and 14.8 kcal mole^{-1} for di-n-butylamine[22]. Since the reaction of benzoyl peroxide with tertiary amines, for example dimethylaniline, has a chain mechanism, the problem arises whether the mechanism of its reactions with secondary and primary amines is also of the same type. It was shown[20] that the addition of DPPH-H does not affect the rate of reactions of benzoyl peroxide with diphenylamine, although DPPH-H is then converted into DPPH. If this reaction were of the chain type, its rate would decrease in consequence of the formation of the inactive DPPH radicals, incapable of propagating the chain reaction. The absence of an inhibiting effect on addition of isoprene to the benzoyl peroxide–aniline system also indicates that this reaction has a non-chain mechanism. The absence of an isotope effect on replacement in aniline and diphenylamine molecules of a hydrogen atom by deuterium is also contrary to the hypothesis of a chain mechanism for the reaction since in a chain reaction the rate constant ratio k_D/k_H for stage (1) would not be unity. Thus, although the reactions of aniline and diphenylamine with benzoyl peroxide do in fact lead to the formation of free radicals, they are not of chain type.

It is not clear which stage determines the rate of reaction of secondary and primary amines with benzoyl peroxide. The absence of an isotope effect in the reaction of the *N*-deuterated compound[20] is evidence that the transfer of a hydrogen atom or proton from the amine to benzoyl peroxide is not the rate-determining state of the process and it may be that the rate is in fact determined by the transfer of an electron from the amine to the peroxide.

Comparatively little is known about the formation of radicals in the reaction of amines with peroxides of another type—peroxydicarbonates. A striking example illustrating the possibility, in principle, of the formation of radicals in this system is the observation by Vasil'ev and Nalbandyan[24] of chemiluminescence in the visible part of the spectrum arising from interaction between dimethylaniline and dicyclohexyl peroxydicarbonate (CPC) at 20°C in benzene. It was shown that, in the absence of oxygen, the chemiluminescence intensity I is a maximum at the instant of mixing of the reactants and decreases according to the law $I^{-1/2} = I_0^{-1/2} + dt$, which can be readily derived on the hypothesis that the excited product is formed via a bimolecular reaction between dimethylaniline and dicyclohexyl peroxydicarbonate.

Razuvaev et al.[25] analysed the products of this reaction and isolated 1.97 moles of CO_2, 0.88 mole of cyclohexanol, and 0.8 mole of *N*-cyclohexyloxylmethyl-*N*-methylaniline per mole of decomposed dicyclohexyl peroxydicarbonate. On the basis of the composition of the products, a reaction mechanism, analogous to Horner's mechanism for benzoyl peroxide, was proposed:



Since the reaction product is a highly luminescent amine derivative, one may suppose that this compound, formed by radical recombination, in fact serves as the chemiluminescence emitter.

The energy relations of this reaction have not been investigated at all. It is only known that the reaction of di-isopropyl peroxydicarbonate with methyldiphenylamine is described by an Arrhenius temperature equation of the type

$$k = 10^{11} \exp(-19\,400/RT) \text{ litre mole}^{-1}\text{ s}^{-1}.$$ [26]

The oxidation of aromatic amines by organic peracids, which yields amine oxides (in the case of tertiary amines) or phenylhydroxylamines and nitroso-, nitro-, azo-, and azoxy-compounds (in the case of primary and secondary amines), has been for a long time a well known synthetic reaction (its chemistry was described in detail in other reviews[27,28]).

The results of the kinetic analysis of these reactions [second kinetic order, low activation energies (about 13 kcal mole^{-1}) and the absence of an effect of methyl methacrylate (MMA) on the rate] can be accounted for by a nucleophilic mechanism[27,29].

Rassat and coworkers[30] investigated by ESR the intermediate products in the oxidation of a large class of primary, secondary, and tertiary aromatic and heterocyclic amines by *p*-nitro- and *m*-chloro-perbenzoic acids in various solvents: in all cases these proved to be nitroxide radicals. However, the pathways in the formation of these radicals are obscure; it is only clear that they are secondary products derived from the amines. Thus it is at present difficult to arrive at an unambiguous conclusion concerning the applicability of the radical mechanism to the oxidation of amines by peracids solely on the basis of the detection of nitroxide radicals, although this mechanism is not inconsistent with the results of kinetic analysis.

Hydroperoxides also react readily with amines and are at the same time reduced into the corresponding alcohols in fairly high yields (72–100%)[31]. The composition of the amine oxidation products is complex and depends on the nature of the amine[32].

The reactions of cumenyl peroxide with phenothiazine, its 3,3-dimethoxy-derivative, and diphenylamine have been investigated by ESR[33] in deoxygenated (to a residual pressure of 10^{-2} mmHg) benzene solutions between 20° and 160°C. The formation of nitrogen radicals derived from phenothiazine and its derivative was observed even at room temperature. When the thioamine was taken in an excess (100:1 or 10:1) there were no changes in the ESR spectra of these "primary" radicals even on heating to 60–70°C. In the presence of an excess of the hydroperoxide and at 60–70°C the "primary" nitrogen radicals were gradually converted into the "secondary" nitroxide radicals, probably via the mechanism

$$Ar_2\dot{N} + R'OOH \rightarrow Ar_2N{-}OH + R'\dot{O}\,, \qquad (3)$$

$$Ar_2N{-}OH + R'OOH \rightarrow Ar_2N{-}\dot{O} + H_2O + R'\dot{O}\,. \qquad (4)$$

The ESR spectra of the "primary" and "secondary" thioamine radicals differ significantly in the splitting (a_N^{sec} is greater by about 30% than a_N^{prim}), in the nature of the hyperfine structure (HFS), and in the values of the *g*-factors ($g^{prim} = 2.0029$ and $g^{sec} = 2.0038$). With diphenylamine, the nitroxide radicals are detected immediately.

The formation of nitroxide radicals in 100% yield was also observed by Coppinger and Swalen[34] using ESR in the oxidation of a large class of secondary and tertiary aliphatic and secondary aromatic amines by *t*-butyl hydroperoxide (TBHP). These results convincingly demonstrate that nitroxide radicals are formed in all cases according to the mechanism represented by reactions (3) and (4).

The mechanism of the primary elementary steps in the interaction of hydroperoxides with amines remains obscure. It has been suggested that[33] nitrogen radicals are formed from amines by a molecular mechanism:

$$Ar_2NH + R'OOH \rightarrow Ar_2\dot{N} + H_2O + R'\dot{O}\,.$$

A similar mechanism was considered, for substituted hydrazines alone, also by Maruyama et al.[35] When t-butyl hydroperoxide was allowed to react with DPPH-H in benzene at 60°C, they detected and identified by hydrazyls radicals, by comparing the hyperfine structure and the overall width of their ESR spectrum with that of a standard—DPPH radicals. Triphenylhydrazine was oxidised under milder conditions (4°C) and the reaction was accompanied by the successive appearance of three types of ESR spectra, which were attributed respectively to the radicals Ph_2-NPh, PhN-OH, and $Ph_2N\dot{O}$. However, the interpretation of the ESR spectra of the first two radicals gives rise to doubts and consequently the assignment of the spectra to the above products cannot be regarded as unambiguous.

The kinetics of the reactions of hydroperoxides with amines have been investigated in a number of studies. It was shown that the rates of these reactions are

described by second-order kinetic equations; the results of the kinetic analysis are presented in Table 1.

It follows from the analysis of the literature data that the formal kinetics of the reactions of peroxy-compounds with aromatic amines and the composition of the reaction products have been fairly adequately investigated; there is a need for a revision of only the fundamental aspect of the mechanism—the detection and identification of the primary radical-cations derived from the amines and the interpretation of the reactions of the radicals.

Table 1. Pre-exponential factors and the activation energies for the reactions of amines with hydroperoxides.

Amine	Hydroperoxide	Solvent	k_0, litre, mole^{-1} s^{-1}	E_{act}, kcal mole^{-1}	Refs.
Diethylamine	cumenyl hydroperoxide	Water	$8.7 \cdot 10^9$	17.0	36
Triethylamine	cumenyl hydroperoxide	Water	$5.4 \cdot 10^8$	14.7	37
Pyridine	t-butyl hydroperoxide	Chloro-benzene	$1.9 \cdot 10^7$	21.0	38
Triphenylhydrazine	t-butyl hydroperoxide	Benzene	$0.2 \cdot 10^2$	5.6	35*
N-cyclohexyl-*N'*-phenyl-*P*-phenylene-diamine	polypropylene hydroperoxide	Solid phase	$1.3 \cdot 10^5$	13.0	39

* The values of k_0 and E_{act} were determined by the present authors from the data of Maruyama et al.[35]

The results of experiments[40-42] unambiguously confirm the existence of a one-electron amine oxidation stage, i.e. the stage involving the formation of radical-cations; this is clearly confirmed by the observation of the ESR spectra of the radical-cations of dimethylaniline, *NNN'N'*-tetramethyl-*p*-phenylenediamine, 2,2',4,4',6,6'-hexamethoxydiphenylamine, *p*-phenylenediamine, and *N*-isopropyl-*N'*-phenyl-*p*-phenylenediamine formed in the reactions with various peroxy-compounds: benzoyl peroxide, dicyclohexyl peroxydicarbonate, t-butyl hydroperoxide, and olefin ozonides†. The isotropic and anisotropic hyperfine coupling constants for the ^{14}N nuclei and protons of the amino-groups and aromatic rings and also the unpaired electron densities were determined.

For example, the radical-cation derived from dimethylaniline gives rise to an ESR spectrum with a complex hyperfine structure due to the coupling of the unpaired electron with the nitrogen nucleus (a_N = 10.0 Oe), the protons of the methyl groups ($a_{H(NCH_3)}$ = 11.8 Oe), and the *ortho*- (a_H^o = 1.7 Oe), *meta*- (a_H^m = 0.8), and *para*-protons (a_H^p = 5.2 Oe) of the aromatic ring.

It is noteworthy that the observed constant a_N is in good agreement with data[43-45] for the radical-cations derived from *para*-substituted dimethylanilines formed on oxidation of the amines by Ce^{4+} ions in a flow system[43] or electrochemically[44,45]. Table 2 lists the hyperfine coupling constants for the ^{14}N nucleii of the radical-cations of dimethylaniline and its *para*-derivatives (in oersteds); evidently the constants a_N are correlated with Hammett's σ parameters, the relation being linear (Fig. 1).

† The reaction of amines with ozonides had not been reported previously.

Subsequently the electronic structure of the dimethylaniline radical-cation was calculated[45] by the Hückel molecular orbital method. The Coulombic and exchange integrals for the nitrogen atoms were assumed to be given by expressions of the form $\alpha_N = \alpha_C + 0.50\beta_{CC}$ and $\beta_{CN} = \beta_{CC}$. The calculated unpaired electron density at the nitrogen atom ρ_π^N proved to be 0.5181. Using this theoretical value of ρ_π^N, the a_N constant for the dimethylaniline radical-cation can be estimated with the aid of the familiar relation $a_N = Q_N \rho_\pi^N$ (where Q_N = 20.6 Oe).[46] The result is a_N = 10.7 Oe, which is very close to the experimental value in Table 2.

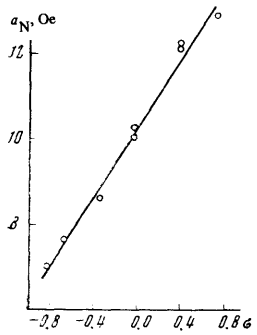


Figure 1. a_N/σ diagram for the hyperfine coupling constant of the radical-cations of dimethylaniline and its *para*-derivatives.

Table 2. The values of a_N (in oersteds) for the radical-cations of dimethylaniline and its *para*-derivatives.

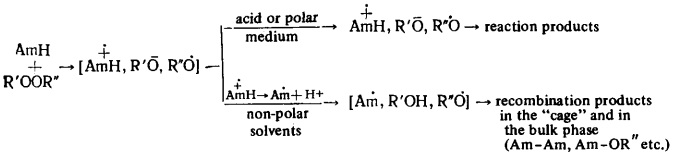
Compound	a_N, Oe	δ_{para}	References
$(CH_3)_2\dot{N}^+$—C$_6$H$_4$—$N(CH_3)_2$	6.99	−0.83	44
$(CH_3)_2\dot{N}^+$—C$_6$H$_4$—NH_2	7.62	−0.66	45
$(CH_3)_2\dot{N}^+$—C$_6$H$_4$—OH	8.6	−0.32	43
$(CH_3)_2\dot{N}^+$—C$_6$H$_5$	10.0	0.0	43, 44
$(CH_3)_2\dot{N}^+$—C$_6$H$_4$—$NHCOCH_3$	10.24	0.0	45
$(CH_3)_2\dot{N}^+$—C$_6$H$_4$—CHO	12.1	0.45	45
$(CH_3)_2\dot{N}^+$—C$_6$H$_4$—$COOC_2H_5$	12.14	0.45	45
$(CH_3)_2\dot{N}^+$—C$_6$H$_4$—NO_2	12.8	0.78	45

In the ESR spectrum of the radical cation of another amine (2,2',4,4',6,6'-hexamethoxydiphenylamine) there are four lines with intensity ratios close to 1 : 2 : 2 : 1, due to the coupling of the unpaired electron with the ^{14}N nucleus and the NH proton, which are approximately equivalent (a_N = 7.5 Oe and $a_{H(NH)}$ = 8.1 Oe). This radical-cation is very stable: it is clearly detected over a period of several days and in acid media its yield is close to 10%.

The radical-cations derived from amines have been investigated in various solvents. In non-polar solvents the radical-cations are usually unstable and undergo secondary reactions. The sequence of these reactions is well illustrated by the following example.

The radical-cation is deprotonated to give a nitrogen radical. The ESR spectrum of the latter is a 1 : 1 : 1 triplet due to the coupling of the unpaired electron with the nitrogen nucleus (a_N = 8.1 Oe). These nitrogen radicals then recombine to give hydrazine. As a result of a secondary electron transfer from hydrazine to the peroxide or the primary radical-cation, a secondary hydrazine radical-cation is produced. Its ESR spectrum at 20°C and at 77°K consist of five lines due to the coupling of the unpaired electron with the two equivalent nitrogen nuclei. The isotropic hyperfine coupling constant for this radical-cation is 6.6 Oe, the anisotropic coupling constant is 5.2 Oe, and the unpaired electron density at each nitrogen atom is 0.41. [41]

Analysis of the structures of the radical-cations and their reactions enabled the authors [40,41] to propose the following general mechanism for the reaction of peroxy-compounds with aromatic amines:



The mechanism includes electron transfer from the amine to the peroxide and the formation of an ion-radical pair. In acid and polar media the radical-cations are stabilised. In non-polar solvents the radical-cations are deprotonated to give radical products.

The effectiveness of the initiation of polymerisation by the amine–peroxide system may be accounted for by this mechanism: it is determined by the relative probabilities of the release of an individual radical into the bulk phase and of the transfer of a proton from the radical-cation to the anion with subsequent recombination of the radical pair within the cage.

Thus the detection by ESR of the radical-cations of various aromatic amines [40-42] unambiguously proves the validity of the hypothesis that electron transfer is the first stage of the reaction of amines with various peroxy-compounds: diacyl peroxides, peroxydicarbonates, hydroperoxides, and olefin ozonides. This means that the mechanism of the one-electron oxidation of aromatic amines is probably common to all classes of peroxy-compounds; previously direct evidence had not been obtained for this conclusion. One may suppose that this mechanism is probably valid also for aliphatic amines.

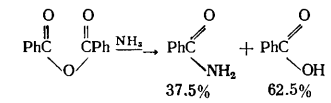
III. KINETICS AND MECHANISM OF REACTIONS OF PHOSPHITES

Whereas the reactions of the majority of peroxy-compounds with amines have been fairly well investigated and there is no doubt that they involve the formation of free radicals, the study of the reactions of peroxy-compounds with phosphites having the general formula $(RO)_3P$ (where R = alkyl or aryl) was until recently restricted solely to stereochemical and isotopic investigations which do not allow unambiguous and reliable conclusions concerning the mechanism of these reactions; moreover, the conclusions concerning the nature of the reactions were frequently made, as will be shown below, on the basis of an analysis of the reactions of phosphite analogues—phosphines R_3P.

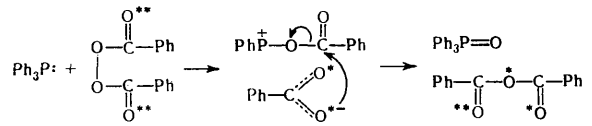
Under mild conditions (at 0°C and below), peroxy-compounds react with phosphines and phosphites to form the corresponding derivatives containing the phosphoryl group P=O (the chemistry of these reactions was described in detail in other reviews [47-51]). The reactions take place with a large heat change (the P=O bond energies are in the range 120–150 kcal mole^{-1} [47,52]). The reactions are also promoted by the easier polarisability of the phosphorus atom compared with the nitrogen atom and possibly $d_\pi - p_\pi$ conjugation, which lowers the energy of the transition state.

Denney and coworkers [53] investigated the mechanism of the reaction of benzoyl peroxide with triphenylphosphine by the isotope tracer method: one of the reactants (benzoyl peroxide) contained ^{18}O in the carbonyl group. It was established that the heavy isotope is fully transferred to only one final product—benzoic anhydride (in the other product, phosphine oxide, there is no ^{18}O). This implies that carbonyl oxygen is not involved in the reaction.

The distribution of ^{18}O in the anhydride was determined by reaction with liquid ammonia. It was found that 37.5% of heavy oxygen is contained in benzamide:



The authors believe that such distribution is possible only when the phosphine attacks the peroxy-oxygen with formation of an ion pair; the latter is converted into the final reaction products by S_N2 nucleophilic substitution:



(* = 1 conventional ^{18}O unit)

An ionic mechanism is also postulated for the reaction of benzoyl peroxide with triallyl phosphite [51] but only on the basis of the usual analysis of the final products (phosphate and anhydride).

However, as in the case of amines, the distribution of ^{18}O in the products of the reaction of benzoyl peroxide with phosphines may be accounted for by the hypothesis of electron transfer as the first stage of the reaction, the isotope tracer method establishing unambiguously only that there is no exchange of carbonyl oxygen atoms without providing more detailed information about the nature of the primary elementary steps of the reactions of peroxides with phosphines and hence also with phosphites.

Among the reactions of phosphites with other peroxy-compounds, those with hydroperoxides are important; the most significant advance achieved is that the mechanism of the elementary stages of these reactions has now been elucidated quantitatively. The first study was published in 1959. Walling and Rabinowitz [54] established that trialkyl phosphites decompose hydroperoxides to a trialkyl phosphate and an alcohol. They suggest that the ion-pair $[(RO_3\overset{+}{P}-OR', {}^-OH]$ is formed as an intermediate. However, Denney et al. [55] believe that the formation of an ion pair of a different structure, $[(RO)_3\overset{+}{P}-OH, {}^-OR']$, converted into the products (phosphate and alcohol) by proton transfer, is more likely. This last hypothesis is based

on the fact that, in the first place, the reduction of hydroperoxides by phosphines in ethanol–$H_2{}^{18}O$ solution yields a phosphine oxide and an alcohol, both without ^{18}O, which can be accounted for by the absence of free OH^- ions and their isotope exchange with the solvent $^{18}OH^-$ ions and, in the second place, by the fact that the optical activity of the initial hydroperoxide is retained in the alcohol formed[56].

However, these arguments put forward by Denney in favour of a nucleophilic mechanism can also be accommodated within the framework of the one-electron mechanism.

Isotope exchange with $^{18}OH^-$ is non-obligatory because the radical–ion pair $[(RO)_3\overset{+}{P}, R'O\bar{O}H]$ can be converted by a monomolecular mechanism into the radical pair $[(RO)_3\dot{P}-OH, R'\dot{O}]$.

Furthermore, the optical activity is retained not only in the $R'O^-$ anions but also in the $R'\dot{O}$ radicals. Thus, in the pyrolysis of the laevorotatory t-butyl α-phenylethyl peroxide in thiophenol, α-phenylethanol is formed[57], i.e. the optical activity does not disappear from the alkoxy-radical‡.

Bearing in mind the unsatisfactory evidence for the mechanism put forward, Denney himself questions it and suggests another mechanism for the initial stage, including the migration of a hydrogen atom in a three-centre activated complex $[R'-\underset{H}{O}\cdots O-P(OR)_3]$. However, this pathway is also unlikely, since it presupposes the dissociation of two bonds simultaneously in a single activated complex. The process most probably consists of a consecutive series of elementary dissociation steps via the intermediate formation of the radicals $R'O$ and $HO\dot{P}(OR)_3$.

On this hypothesis, it was shown[40,59,60] that the introduction of stable iminoxy-radicals, which are powerful free radical acceptors[61], into hydroperoxide–aliphatic phosphite [triethyl phosphite (TEP), tripropyl phosphite (TPP), and iso-octyl diphenyl phosphite] systems leads to their destruction§. This implies that free radicals are formed in the reaction between hydroperoxides and phosphites. The yield of free radicals in the reaction was measured and found to be of the order of 10^{-4}. Direct experiments designed to detect by ESR the free radicals derived from aliphatic phosphites were unsuccessful, probably because of the high rate of destruction of the radicals and their correspondingly low steady-state concentration.

Since the elementary step involving the destruction of radicals is exothermic, the appearance of chemiluminescence in the test system was to be expected; moreover, the energy liberated as a result of these reactions is sufficient for the electronic excitation of their final products [for example, the heat of reaction of triethyl phosphite with t-butyl hydroperoxide, which we estimated as the difference between the heats of formation of the final products (phosphate and alcohol) and the initial reactants, proved to be about 116 kcal mole^{-1}; the values of ΔH_f° for the phosphite and phosphate taken from the literature[62,63] were employed in the calculations].

‡ Recently Bentrude[58] established that the transfer of an oxygen atom from the $R'\dot{O}$ radicals to the optically active phosphines $R_1R_2R_3P$ takes place with retention of the configuration, i.e. the optical activity also does not disappear from the phosphoranyl radical $R_1R_2R_3\dot{P}-OR'$.

§ The experiment designed to investigate the kinetics of the destruction of the acceptor (at 20°C in benzene) was performed on an EPR-2 IKhF spectrometer.

Indeed a luminescence was observed[40,64] in the reaction of t-butyl hydroperoxide with triethyl phosphite and tripropyl phosphite in benzene at 20°C in the absence of oxygen. It was found that the luminescence intensity and the reaction rate constant did not change in the presence of stable iminoxy-radicals; the acceptor was employed at concentrations which were the same as those in the experiments where it was shown by ESR[59] that it captures completely all the radicals released into the bulk phase. This result is important; it implies that the excitation step is not influenced by additional active components of the chemical system, i.e. the emitter (this proved to be the triplet molecule of the reaction product—phosphate[64]) appears in the exothermic step involving the destruction of the free radicals $R'\dot{O}$ and $HO\dot{P}(OR)_3$, which does not take place in the bulk phase but in the "cage" where they are formed.

Thus the chemiluminescence observed in the reaction of t-butyl hydroperoxide with phosphites is a source of information about the processes within the cage.

The question arises of the causes of the low number of radicals released from the cage into the bulk phase (about 10^{-4} of the number of hydroperoxide molecules which have reacted). One of these is probably the small distances between the radicals in the cage.

The cage effect is known[65] to depend strongly on the "diameter" of the cage, i.e. on the distance r_0 between the centres of the radicals of the pair at the instant of its formation. Thus in the thermal decomposition (at 65°C) of diacetyl peroxide, where the CH_3 radicals recombining in the cage are separated by two large CO_2 molecules, the yield of ethane (a measure of the cage effect) is 6% and in the photolysis of azomethane, where the methyl radicals are separated only by an N_2 molecule, the yield of ethane is higher by a factor of 10 (65%). Consequently in the absence of inert molecules the radicals in the $[(RO)_3(OH)\dot{P}\ \dot{O}R']$ pair may be side by side and the probability of the cage effect becomes close to unity.

Another kinetic cause of the low number of radicals liberated from the cage may be the high rate of their disproportionation to the reaction products—phosphate and alcohol; the rate constant for this process may be estimated from the experimental data obtained in the present author's study[40] characterising the dependence of the cage effect in the reactions of t-butyl hydroperoxide with triethyl and tripropyl phosphites on the viscosity of the solvent and temperature.

Since it was established[40] that the radicals are released into the bulk phase only by diffusion (the activation energy for the liberation process $E_f \simeq 2.9$ kcal mole^{-1}, a typical value for the activation energy for the diffusion of species in a liquid[66]), in this case the probability of their release is

$$f = \frac{k_{diss}}{k_{diss} + k_{chem}},$$

and its ratio to the probability of disproportionation in the cage is given by

$$\frac{f}{1-f} = \frac{k_{diss}}{k_{chem}}, \qquad (I)$$

where k_{diss} is the rate constant for the dissociation of the pair (s^{-1}) and k_{chem} the rate constant for the chemical monomolecular conversion of the pair into the reaction products (s^{-1}), i.e. the reciprocal of the lifetime of the

pair. Within the framework of the hydrodynamic Stokes–Einstein model, the viscosity and the rate constant for the dissociation of the pair are related by the expression[67]

$$k_{diss} = \frac{6D}{r_0^2} = \frac{kT}{\pi r_0^3 \eta},$$

where η is the viscosity of the medium and D the diffusion coefficient. Since the probability f of the release of radicals from the cage into the bulk phase is smaller by approximately four powers of ten than the probability of the chemical reaction of the pair, Eqn.(I) simplifies to

$$f \simeq \frac{k_{diss}}{k_{chem}},$$

whence after substituting the expression for k_{diss}, it is possible to obtain a relation between f and the viscosity of the solvent at a constant temperature:

$$f = \frac{kT}{\pi r_0^3 k_{chem}} \cdot \eta^{-1} \qquad (II)$$

and between f and T/η at different temperatures in the same solvent:

$$f = \frac{k}{\pi r_0^3 k_{chem}} \cdot T/\eta \qquad (III)$$

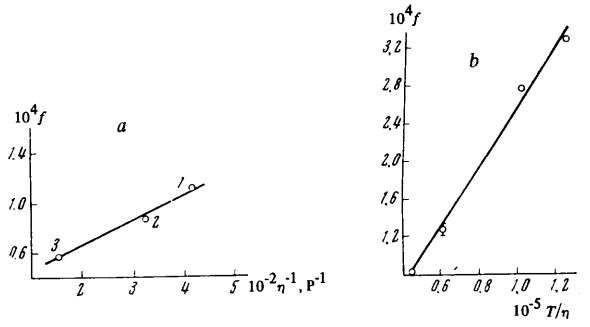


Figure 2. Variation of the number of radicals liberated from the cage into the bulk phase: *a*) with the viscosity of the solvent [according to Eqn. (II)] [1) pentane; 2) hexane; 3) benzene (reaction of t-butyl hydroperoxide with triethyl phosphite at 20°C)]; *b*) with T/η [according to Eqn. (III)] (reaction of t-butyl hydroperoxide with tripropyl phosphite in hexane between −30° and +42°C).

Fig. 2 shows that these formulae hold fairly well under experimental conditions. It follows from both plots that, for an average cage diameter $r_0 = 15$ Å, the rate constant is 1.6×10^{13} s^{-1} (for the reaction with triethyl phosphite) and 4×10^{12} s^{-1} (for the reaction with tripropyl phosphite); these values are close to the frequency of monomolecular decomposition steps; moreover, the linearity of the relation between f and η^{-1} (T = const.) and T/η shows that the rate constant for the disproportionation of radicals within the cage is virtually independent of temperature, as was in fact to be expected.

The kinetic mechanism of the formation of radicals in the reaction of hydroperoxides with aliphatic phosphites can be represented in the following way in a general form:

$$R'OOH + (RO)_3P \xrightarrow{k} \{[R'\dot{O}\overset{+}{O}H \cdots \overset{+}{P}(OR)_3] \rightarrow R'\dot{O}\dot{P}(OH)(OR)_3\} \rightarrow \begin{cases} \xrightarrow{(1-f)k} R'OH + O{=}P(OR)_3 \\ \xrightarrow{fk} R'\dot{O} + \dot{P}(OH)(OR)_3 . \end{cases}$$

In the first stage an electron is transferred from the phosphite to the hydroperoxide with formation of an ion–radical pair; the latter is unstable in neutral solvents and undergoes a monomolecular conversion into a radical pair. The pair disappears mainly by disproportionation within the cage to molecular products—phosphate and alcohol. This mechanism is confirmed by data for radical accepting reactions and chemiluminescence¶; moreover, the idea of electron transfer as the first stage of such reactions is consistent with the capacity of aliphatic phosphites to form paramagnetic charge-transfer complexes (CTC) with typical electron acceptors such as *p*-chloranil[71] trifluoronitrosomethane[72], and others.

Thus the low number of radicals released into the bulk phase (about 10^{-4}) can be explained by such a latent radical mechanism. However, it should be noted that such a low yield may be interpreted also in a different way. It may be assumed that the reaction takes place mainly by non-radical, i.e. ionic or molecular, mechanisms and the contribution of the radical pathway is small (about 10^{-4}). Both alternatives are equivalent in the kinetic sense; therefore, other criteria which would allow a choice will be examined.

One of the characteristics of liquid-phase radical reactions is known to be[73] the cage effect. This effect is associated with the mobility of the species in the liquid phase. Therefore, within the framework of the Stokes–Einstein model, a dependence of the yield of radicals on the viscosity of the solvent is to be expected. Indeed such dependence is found in the reactions of phosphites with hydroperoxides[40,59].

Secondly, the activation energy for the liberation of radicals from the cage into the bulk phase should be close to the activation energy for the diffusion of radicals in the liquid, i.e. 2–4 kcal mole^{-1}.[73] In the reaction of phosphites (tripropyl phosphite in hexane) this energy is 2.9 kcal mole^{-1}.[40]

Thirdly, if the rate constant for the main process is the same in two different solvents with similar viscosities (benzene and styrene) but the yield of radicals in one of them is much higher (more than a factor of ten[59]), one may suppose that the contribution by the radical pathway is much greater. This finding cannot be accounted for without adopting a radical mechanism. It appears that in styrene a new mechanism of the liberation of radicals from the cage, a chemical relay mechanism, obtains; moreover, styrene may affect the lifetime of the radical pair owing to solvation effects.

¶ In principle, the formation of a radical with an unpaired electron at the phosphorus atom as a kinetically independent species is possible also in the reactions of trialkyl phosphites with free radicals, in particular with t-BuO· radicals. Recently this was confirmed experimentally by the observation of the chemically induced polarisation of ^{31}P nuclei in trialkyl phosphates and dialkyl phosphonates[68], by the observation of the ESR spectra of t-butyl radicals[69] as the decomposition products of the primary phosphoranyl radicals $(RO)_3\dot{P}$–O–t-Bu, and also by the analysis of the distribution of the ^{14}C isotope label in tri-t-butyl phosphate[70].

Furthermore, the finding that the chemiluminescence emitter arises in the cage and not in the bulk phase may serve as evidence that mainly radical processes occur in the cage. However, for a clear understanding of the mechanism of the step in which the emitter is formed, analysis of its excited state is necessary. It was found[64] that, in the reaction of t-butyl hydroperoxide with triethyl phosphite, the phosphate molecule in a triplet state is the chemiluminescence emitter. This finding may be regarded as evidence that the chemiluminescence is a result of the reaction of free radicals only. The following considerations lead to this conclusion. We shall assume that the luminescence arises in the ionic reaction $R'O^- + \overset{+}{H}OP(OR)_3 \rightarrow R'OH + O{=}P(OR)_3$ (according to Denney[55]) as a result of proton transfer from the cation to the anion $R'O^-$. The proton in the cation is weakly bound to the oxygen atom via the lone electron pair of the latter; this means that the P=O bond in the cation already exists and is weakly perturbed by the proton. Therefore the anion, on coming into contact with the cation, "abstracts" the proton, so that the energy of the phosphate molecule produced in this process hardly changes. As a result of this, the entire energy liberated in the recombination of $R'O^-$ and the proton is localised at the alcohol molecule and there is a high probability of its degradation via the internal degrees of freedom. Thus, within the framework of Denney's ionic mechanism, it is difficult to explain the excitation of the phosphate molecule. The localisation of the electron excitation energy at the phosphate molecule is to be expected in the disproportionation of the $R'\dot{O}$ and $HO\dot{P}(OR)_3$ radicals, where the abstraction of a hydrogen atom may lead to the triplet excitation of the double bond in the phosphate.

Finally we may recall that low yields of radicals (about 10^{-3}) are observed also in the benzoyl peroxide–diphenylamine system; this finding was also explained[20] by the high rate of recombination of nitrogen and benzoate radicals in the cage. In this case there is no doubt that the reaction proceeds wholely by a radical mechanism. As will be shown below, in this sense the reactions of amines, phosphites, and also sulphides have common properties and common characteristics.

Thus all the above criteria suggest a latent radical mechanism of the reactions of hydroperoxides with aliphatic phosphites.

Within the framework of the concept of the latent radical mechanism, the mutual enhancement of the effectiveness of phenols and phosphites in the inhibition of the oxidation of polymers can be accounted for[60]; it is due to the high effectiveness of the phosphites in the suppression of degenerate branching.

The kinetics of the reactions of hydroperoxides with aliphatic, aromatic, and mixed phosphites have been investigated in a number of studies by measuring the consumption of the hydroperoxide[59,74,75] and stable radicals[59,60] and by following the chemiluminescence, which was first observed[64] in these reactions. It was found that the rates of the reactions are described by a first-order kinetic equation with respect to each component. Thus the rate constant for the reaction of tri-t-butylphenylphenylene phosphite with 1,1-diphenylethyl hydroperoxide in benzene is described by an equation of the form $k = 2.4 \times 10^8 \exp(-14\,000/RT)$ litre mole^{-1} s^{-1}†; the following expression was obtained for the rate constant for the reaction of tripropyl phosphite with *t*-butyl hydroperoxide in hexane[40]: $k = (0.5 \pm 0.1) \times 10^2 \exp(-5200 \pm 1400/RT)$ litre mole^{-1} s^{-1}. Evidently, as in the case of amines, the reactions of phosphites with hydroperoxides have low activation energies.

† We estimated the values of k_0 and E_{act} from Mukmeneva's data[74].

IV. KINETICS AND MECHANISM OF REACTIONS OF SULPHIDES

We shall now consider the reactions involving sulphides which probably constitute yet another example of oxidation–reduction reactions of peroxy-compounds. In the literature there are several examples confirming this hypothesis. Thus in a study of the effectiveness of the initiation of the polymerisation of methyl methacrylate by various hydroperoxides, Minoura et al.[76] observed an acceleration of the process by the addition of dibenzyl sulphide at 50°C. Kinetic analysis showed that the rate of polymerisation is given by

$$w_n = (k_p/k_t^{1/2})[MMA]^{1.3}[R_2S]^{1/4}[R'OOH]^{1/2}.$$

This shows that the free radicals initiating the polymerisation of methyl methacrylate are formed in a bimolecular reaction of the hydroperoxide and the sulphide; however, it should be noted that Minoura et al.[76] did not estimate the effectiveness of such initiation.

The yield of free radicals in the reactions of hydroperoxides with sulphides (dilauryl thiodipropionate and dibenzyl sulphide) was first measured by Pobedimskii and Buchachenko[77] by the method of stable iminoxy-radicals; it proved to be low (about 10^{-4}). Pobedimskii and Buchachenko[77] suggested a kinetic mechanism for the reaction analogous to that used for the reactions of phosphite[59] (see p. 23). As for phosphites, the low yield of radicals in the reactions of sulphides with hydroperoxides can be accounted for by the closeness of the radicals in the pair and the high rate of their disproportionation to the reaction products; even the addition of radicals to the double bond cannot compete, in terms of rate, with the process taking place within the cage. Thus in styrene, where the rate constant is the same as in benzene, the yield of radicals at 20°C was 3.3×10^{-3}. This example and also the data showing the low yield of radicals in the reactions of amines and phosphites[20,59] illustrate the common latent radical nature of the reactions of sulphides, phosphites, and aromatic amines with peroxy-compounds.

Subsequently Schmidt et al.[78] observed by ESR the formation of the radical-cations of derivatives of diphenyl sulphide [di-(4-methylphenyl), di-(4-methoxyphenyl), di-(4-methoxy-3-methyl), di-(2-chloro-4-methoxyphenyl), di-(4-hydroxyphenyl), di-(3,6-dichloro-4-hydroxyphenyl), and di-(6-chloro-4-hydroxyphenyl) sulphides] in their oxidation by persulphate ions in concentrated sulphuric acid solution at 20°C. For example, the ESR spectrum of the radical-cation of di-(4-methoxyphenyl) sulphide (*g*-factor = 2.0079) consists of nine lines with a splitting of 1.25 Oe owing to the coupling of the unpaired electron with the eight equivalent protons of the aromatic rings (probably the unpaired electron density at the *ortho*- and *meta*-protons is the same); the observed ratios of the hyperfine structure intensities (0.6 : 7 : 27 : 54 : 70 : 53 : 23 : 4 : 0.6) proved to be close to the ratios expected for the proton structure (1 : 8 : 28 : 56 : 70 : 56 : 28 : 8 : 1). The isolation of the radical-cations in a pure state in 100%

yield (as the hexachlorostannate) unambiguously demonstrates that the reaction investigated takes place exclusively via one-electron transfer.

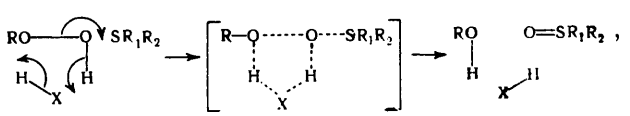
The radical cations $CH_3O-C_6H_4-\overset{+\cdot}{S}-C_6H_4-OCH_3$

were detected[77] also in the reactions of cumenyl peroxide, benzoyl peroxide, and dicyclohexyl peroxydicarbonate with the initial sulphide in trifluoroacetic acid and in its mixtures with polar solvents (i.e. in media where the radical cations are stabilised). The experimental hyperfine coupling constants ($a_H^o = a_H^m = 1.35$ Oe) are close to those measured for the same radical-cations obtained in the oxidation by persulphate ions[78]. This result is important; it can be regarded as confirmation of the suggested mechanism for the formation of free radicals in the reaction of hydroperoxides with aliphatic sulphides[77].

In a number of studies the products and the kinetics of the reactions of peroxy-compounds (diacyl peroxides, peracids, and hydroperoxides) with sulphides were investigated. At moderate temperatures benzoyl peroxide and hydroperoxides usually yield only the sulphoxides $R_2S{=}O$, whereas peracids convert sulphides via sulphoxides into sulphones R_2SO_2.[27,28,79] The rates of these two stages differ significantly; for example, peracetic acid in acetic acid solution oxidises diphenyl sulphide to the sulphoxide about 1000 times faster than the oxidation of the sulphoxide to the sulphone[80]. Horner[81,82] showed that the reactions of sulphides with benzoyl peroxide in chloroform are described by a second-order kinetic equation; aliphatic sulphides reacted at 20°C faster than aromatic sulphides [the rate constant for the reaction of $(C_2H_5)_2S$ is about 3.6×10^{-3} litre mole^{-1} s^{-1} and that for the reaction of $C_2H_5SC_6H_5$ is 4.5×10^{-4} litre mole^{-1} s^{-1}]. Overberger and Cummins[83] found that the reduction of peracids by sulphides also follows second-order kinetics.

The kinetics of the reaction of hydroperoxides with sulphides were investigated in protic and aprotic solvents simultaneously by iodometric titration of the hydroperoxide and chemical determination of the reaction product (the sulphoxide)[27,28,79,84,85]. In alcoholic, aqueous alcoholic, acidic, and basic solutions at temperatures between −65° and +75°C the reaction has the following parameters: (1) 1 : 1 stoichiometry according to the equation $R_2S + R'OOH \rightarrow R_2SO + R'OH$; (2) first order with respect to each component; (3) low activation energies (between 9.5 and 17.5 kcal mole^{-1} depending on the structure of the hydroperoxide[79]; (4) specific Brönsted acid catalysis at pH < 3.[85]

In aprotic solvents unusual kinetic relations were observed. Thus Bateman and Hargrave[84] found that the rate of the reaction of cyclohexyl methyl sulphide with t-butyl hydroperoxide in benzene at 50°C obeys a second-order kinetic equation with respect to the hydroperoxide, while in a benzene–acetic acid (or alcohol) mixture the hydroperoxide is consumed according to first-order kinetics. It was suggested[79,84] that this reaction has a molecular mechanism without the formation of free radicals, via the transfer of a hydrogen atom in a cyclic activated complex:



where X = CH_3COO, ROO, or RO.

However, many facts cannot be explained by the proposed mechanism[79,84] [different kinetic effects of the hydrogen bonds between the hydroperoxide and the molecules of the medium (methanol or acetic acid), unequal effects of the inhibitors and oxygen on the rate of reaction as a function of the solvent, fractional order of the reaction with respect to the sulphide in the absence of oxygen, etc.] and therefore the findings in these investigations cannot be regarded as unambiguous. Moreover, the destruction of stable radicals following their introduction into the hydroperoxide–sulphide system (in the presence of the sulphide alone or the hydroperoxide alone, stable radicals are not consumed)[77] and also the initiation of the radical polymerisation of methyl methacrylate by a hydroperoxide–sulphide system[76] are completely inconsistent with the hypothesis of a molecular mechanism; moreover, the type of relation between w_n and the concentrations of the sulphide and the hydroperoxide corresponds to bimolecular formation of radicals (and not trimolecular as would be expected according to Bateman and Hargrave[84]). A polarographic study of the consumption of t-butyl hydroperoxide in the reaction with dilauryl thiodipropionate at 20°C in benzene also led the authors[77] to the conclusion that the reaction in benzene is of first order with respect to each component.

Thus the detection of radical-cations and free radicals in various sulphide–peroxy-compound systems permits the hypothesis of the existence of a single mechanism for all the reactions of sulphides: it suggests that the reactions following electron transfer have a radical mechanism. Within the framework of these concepts, it is possible to explain also the significance of the specific acid catalysis of the reactions of sulphides with hydroperoxides[85]; it is probably due to the fact that electron transfer from the sulphide molecule to the hydroperoxide takes place with participation of the protonated form of the latter, which is more reactive (a more powerful electron acceptor) than the free hydroperoxide.

V. OXIDATION–REDUCTION NATURE OF THE REACTIONS OF PEROXY-COMPOUNDS WITH PHOSPHITES, SULPHIDES, AND AROMATIC AMINES

An interesting and general result of the reactions of peroxy-compounds with amines, phosphines (and hence also phosphites), and sulphides is, as shown below, the existence of correlations of the Hammett equation type for the rates of these reactions and also correlations between the rate constants and ionisation potentials and electron affinities; the occurrence of identical correlations implies that the mechanisms of all three types of reaction are governed by a common relation. We shall examine these correlations and shall attempt to account for them in terms of an oxidation–reduction mechanism.

From the standpoint of Mulliken's theory[86], electron transfer in a donor–acceptor pair takes place between the higher filled molecular orbital (MO) of the donor and the lower vacant molecular orbital of the acceptor. Calculation of the electronic structures of the various peroxy-compounds by the extended Hückel method[87-89] showed that the lower vacant molecular orbital of these compounds is an antibonding orbital localised in the $2p\sigma$-orbital between two oxygen atoms.

One may suppose that the introduction of electron-accepting substituents into the peroxide and of electron-donating substituents into the donor molecule will lead respectively to a decrease of the energy level of the

antibonding orbital along the O–O bond in the peroxide and to an increase of the level of the donor orbital filled by the lone electron pair.

Bearing in mind that the rates of the reactions of peroxy-compounds with amines, phosphites (phosphines), and sulphides are probably determined by electron transfer from the donor to the peroxide, such mutual approach of the energy levels of the reactants on introduction of polar groups will result in a lowering of the activation energy for the process and hence in an increase of its rate constant.

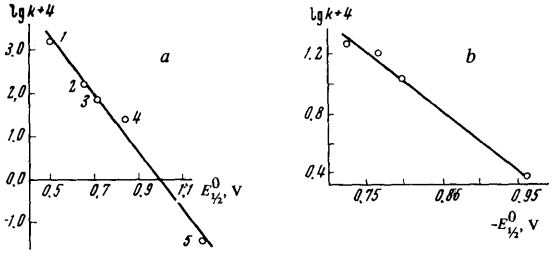


Figure 3. Variation of the logarithm of the rate constant: *a*) with the half-wave oxidation potential for the reaction of benzoyl peroxide with dimethylaniline and its *para*-derivatives [1) CH_3O; 2) CH_3; 3) H; 4) Cl; 5) NO_2]; *b*) with the half-wave reduction potential for the reaction of cyclohexyl methyl sulphide with various hydroperoxides.

Indeed the literature data show that many of the reactions considered here obey the Hammett relation. For example, electron-donating substituents in the benzoyl peroxide molecule decrease the rate of its reaction with dimethylaniline ($\rho = +0.181$).[14] The effect of the substituents in the ring of the dimethylaniline molecule on its reaction with benzoyl peroxide is of the opposite type ($\rho = -4.25$; this value was determined by the present authors from the data of Horner and Scherf[81] for σ° in the range between −0.27 and +1.27‡); then the rates of the reactions of amines with the most electron-accepting and electron-donating substituents differ by a factor not less than 10^3§. Ring substituents have an analogous effect on the rate of reaction of methyl phenyl sulphide with benzoyl peroxide: in the extreme cases the rates of reaction differ by a factor of about 200.[82] However, the slope of the correlation line was smaller ($\rho = -2.2$; this value was determined by the present authors from the data of Horner and Jügens[82] with σ° in the range between −0.27 and +0.78); probably, the effect of substituents on the position of the donor level in the sulphide is somewhat reduced compared with the analogous effect in the amine. Finally, it is known[49] that the reaction of phosphines and benzoyl peroxide is also accelerated by the introduction into the peroxide molecule of electron-accepting substituents.

The rates of the reactions of benzoyl peroxide with dimethylaniline and its *para*-substituted derivatives show an explicit relation also with the polarographic oxidation potentials of the donor molecules. This relation can be understood if one takes into account the fact that the energies of the highest filled orbitals are frequently correlated with the first polarographic oxidation half-wave potential; in this case such a potential corresponds to the first oxidation stage—the abstraction of one electron from the amine molecule with formation of a radical–cation. Table 3 lists the literature values of the rate constants for the reaction of benzoyl peroxide with dimethylaniline and its *para*-substituted derivatives, the first polarographic half-wave oxidation potentials $E^0_{1/2}$ for which are known.

Table 3. Data for the rates of reaction of benzoyl peroxide with dimethylanilines*.

para-Substituent	$E^0_{1/2}$ (in acetonitrile)	$10^4 k_{20°}$, litre mole^{-1} s^{-1}	Solvent in reaction
CH_3O	0.48	1550	Chloroform
CH_3	0.65	166	ditto
H	0.71	76	»
Cl	0.84	26	»
NO_2	1.19	0.04	»

* The values of k were taken from Horner and Scherf[81] and those of $E^0_{1/2}$ from Seo et al.[92]

Fig. 3 shows the variation of the logarithm of the rate constant with the oxidation half-wave potentials of amines which the present authors plotted from the data in Table 3. Evidently the experimental data fit on a straight line described by the empirical equation $\lg k_1 - \lg k_2 = \alpha(E^0_{1/2(1)} - E^0_{1/2(2)})$, where $\alpha = -6.6$. This relation arises in consequence of the general relation between the affinity of the reaction (the free energy change) and its rate, since the affinity of the reaction in the cases under consideration is determined primarily by the difference between the energies of the lowest vacant molecular orbital of the peroxy-compound and the highest filled molecular orbital of the donor.

Another relation is also to be expected: the relation between the rate constants and the second component of the reaction affinity (the energy of the lowest vacant molecular orbital of the acceptor). The polarographic reduction half-wave potential $E^0_{1/2}$ may serve as a measure for the comparison of the electron-accepting properties. It is known[93] that hydroperoxides are reduced at a dropping mercury electrode by a two-electron process:

$$R'OOH \xrightarrow[+2e^-]{+2H^+} R'OH + H_2O$$

and give rise to a single polarographic wave. If it is assumed that the rate-limiting stage in the electrochemical reduction of the hydroperoxide is the transfer of the first electron, then the experimental value of $E^0_{1/2}$ must correspond to the one-electron reduction of the hydroperoxide $R'OOH + e \rightarrow R'O\dot{O}H$ and consequently can serve

‡ The values of σ° recommended by Taft[90] and Jaffe[91] were employed.

§ Attention should be drawn to the fact that the rate constant for the reaction of benzoyl peroxide with dimethylaniline and its derivatives and the hyperfine coupling constants for the ^{14}N nucleii in the radical-cations (see Fig. 1) vary in the opposite sense on introduction of electron-accepting groups into the aromatic ring; this implies that the a_N/σ correlation has a direct bearing on the reactivity of dimethylaniline and its derivatives.

as a measure of its electron affinity. Using this approximation, we shall attempt to find a relation between the rate constants and the potentials $E^0_{1/2}$.

Comparison of the rate constants for the reactions of various hydroperoxides with cyclohexyl methyl sulphide (Table 4) and the data for their polarographic reduction shows that the rate constant increases as the negative value of $E^0_{1/2}$ diminishes.

Table 4. Data for the rates of reaction of cyclohexyl methyl sulphide with various hydroperoxides (at 50°C in methanol)*.

Hydroperoxide	$E^0_{1/2}$ (in methanol–benzene)	$10^4 k$, litre mole^{-1} s^{-1}	E_{act}, kcal mole^{-1}	$10^{-5} k_0$, litre mole^{-1} s^{-1}
$(CH_3)_3COOH$	−0.96	2.2	14.1	7.6
–OOH	−0.80	10.8	—	—
–OOH	−0.77	16.5	12.6	3.1
–OOH	−0.73	18.4	—	—

* The values of k were taken from Bentrude and Wielesek[70] and those of $E^0_{1/2}$ from Willits et al.[94]

Fig. 3*b* shows this relation in a semilogarithmic form, which, like the relation for the amines (Fig. 3*a*), is satisfactorily consistent with the familiar Dimroth equation[95] for oxidation–reduction reactions: $\lg k_2 - \lg k_1 = \beta(E_2 - E_1)$; for the sulphide, the difference between the redox potentials $E_2 - E_1$ is equivalent to the difference between the reduction half-wave potential $E^0_{1/2(2)} - E^0_{1/2(1)}$ and the slope $\beta = +4.2$.

The existence of Hammett type correlations for the rates of the reactions of peroxy-compounds with amines, phosphines (and, by analogy, with phosphites), and sulphides and also the correlations between the rate constants and the ionisation potentials and electron affinities may serve as an indication that in the activated complex an electron is transferred and that this stage is probably rate-limiting.

In conclusion we may note that many reactions are considered to be ionic or molecular only because free radicals are not detected during their occurrence; in fact, however these reactions can frequently be of the latent radical type, i.e. they can proceed via free radicals which are destroyed in the cage immediately after their formation. Clearly new approaches and new ideas are required in order to be able to control processes within the cage by actively interfering with their kinetics. One of such approaches may be the study of dynamic nuclear polarisation in chemical reactions[96].

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Reactivity and Thermal Stability of Hexafluorides

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The review deals with the possibility of using various physicochemical characteristics of the hexafluorides of *p*, *d*, and *f* elements for a comparative estimation of their thermal stability and reactivity. The force constants of EF_6 molecules, the average bond energy and length, and also the thermodynamic stability constants of the octahedral EF_6 molecules have been used as characteristic properties.
It has been shown that the force constants of the E-F bond are not effective characteristics of the thermal stability and reactivity of all hexafluorides in reactions where more than one E-F bond is dissociated.
Only the thermodynamic stability constants can serve as an objective criterion for the assessment when account is taken of definite dissociation mechanisms of EF_6 molecules (complete or incomplete dissociation).
Within the limits of individual groups of 4*d*, 5*d*, and 5*f* elements and also sulphur, selenium, and tellurium, the variation of the force constants and thermodynamic stability in relation to the incomplete dissociation of the hexafluorides corresponds to the experimental sequences of their thermal stabilities.
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I. INTRODUCTION

Hexafluorides are a class of fluoride compounds formed by certain elements having not less than six *p*, *d*, or *f* valence electrons. Up to the present time, the hexafluorides of 18 elements have been identified: sulphur, chromium, selenium, molybdenum, technetium, ruthenium, rhodium, tellurium, xenon, tungsten, rhenium, osmium, iridium, platinum, polonium, uranium, neptunium, and plutonium. In addition one may expect, by analogy, the formation of the hexafluorides of palladium, iodine, astatine, radon, and americium.

The common properties of hexafluorides are low melting and boiling points and comparatively high volatility under ordinary conditions (Table 1). With the exception of XeF_6, the molecules of hexafluorides EF_6 have the configuration of a regular octahedron belonging to the O_h point group with the element E in the centre. The reactivities of hexafluorides are not the same. Some hexafluorides, for example CrF_6, are so unstable that they can be synthesised and investigated only at very low temperatures, while others (for example sulphur hexafluoride) resemble the noble gases in their chemical inertness.

Hexafluorides have attracted much interest, since those of many elements are obtained and used in individual stages of the technology of the manufacture of nuclear fuel[1-3]. In particular, this accounts for the publication of a large number of studies on the physicochemical properties of both individual hexafluorides and individual groups. Reviews have also appeared on hexafluorides, among which mention should be made in the first place of those by Weinstock[2-4] and O'Donnel and coworkers[5-8].

In Weinstock's work attention was concentrated on the molecular constants of hexafluorides. However, there are certain data on their thermal stabilities[3,4]. O'Donnel and coworkers attempted to make a systematic arrangement of the hexafluorides of certain elements in terms of their reactivities. In particular, they showed that the reactivities of hexafluorides fall on moving down the Groups of the Periodic System, while the thermal stabilities increase on going from elements with 3*d* electrons to elements with 5*d* electrons[5-7].

Table 1. Physicochemical properties of hexafluorides[3,4,8].

Hexafluoride	Type of characteristic electrons of element E	No. of free electrons	Symmetry of ground state of EF_6	M.p., °C	B.p. (sublimation temp.) at p = 1 atm., °C	Critical temp., °C	Vapour pressure at 15°C, mmHg
SF_6	3 *p*	0	A_{1g}	−50.4*	−63.7	45.5	—
SeF_6	4 *p*	—	A_{1g}	−34.7*	−45.9	72.35	—
TeF_6	5 *p*	—	A_{1g}	−37.0*	−38.9	83.25	—
PoF_6	6 *p*	—	A_{1g}	—	—	—	—
CrF_6	3 *d*	0	—	—	—	—	—
MoF_6		0	A_{1g}	17.4	35	—	361
TcF_6	4 *d*	1	$G_{3/2g}$	37.4	55.3	—	135
RuF_6		2	F_{2g}	50.4	45.9	—	58
RhF_6		3	$G_{3/2g}$	70	—	—	38
WF_6		0	A_{1g}	2.0	17.5	—	698
ReF_6	5 *d*	1	$G_{3/2g}$	18.5	33.7	—	358
OsF_6		2	E_g, F_{2g}	32.1	45.9	—	312
IrF_6		3	$G_{3/2g}$	43.8	53.6	177	227
PtF_6		4	A_g	61.3	69.14	—	66
UF_6		0	A_{1g}	64.1**	56.5	245	56
NpF_6	5 *f*	1	$E_{5/2}$ *u*	55.1**	55.2	—	64
PuF_6		2	A_{1g}	51.6**	62.2	—	53
XeF_6		2	—	26	—	—	12

* Under the pressure of its own vapour.
** Triple point.

In the solution of certain practical problems associated with the presence in a chemical system of the hexafluorides of several elements or their lower fluorides, it is necessary to employ some qualitative criterion in order to predict the changes in the system which are potentially possible. Thermodynamic analysis is in many cases impossible, since the thermochemical and thermodynamic constants of many fluorides are unknown. On the other hand, an empirical systematic arrangement may prove to be unreliable, since the rate of a chemical reaction depends on the experimental conditions. For example, in the system "uranium hexafluoride–hydrogen" the products may be uranium pentafluoride, tetrafluoride, trifluoride, or the so called "intermediate" fluorides U_2F_9, U_4F_{17}, etc., depending on the temperature, the reactant ratio, and the effect of light. Until recently it was also believed that molybdenum and tungsten hexafluorides are vigorous fluorinating agents[9,10], but later studies[5,11] showed that these two hexafluorides are inert.

In the present review the possibility of using various physicochemical characteristics of hexafluorides for a comparative estimation of their reactivities and thermal stabilities is discussed. Such characteristics may be the force constants of the EF_6 molecules, the E – F bond energies and lengths, and the equilibrium dissociation constants of hexafluorides. An attempt has been made to discover regularities in thermal stability both for the entire class of hexafluorides and for individual series.

II. PRINCIPAL GROUPS OF HEXAFLUORIDES

Depending on the nature of the valence shell of the element forming the hexafluoride or the type of its valence electrons, all hexafluorides can be arranged systematically in groups according to the position of the elements in the Periodic System. The positions of the hexafluorides of various elements in these groups are consistent with the positions of the elements themselves, either in the Periods (horizontal series) or in the Group (vertical series) of the Periodic System. The horizontal series of hexafluorides comprise the groups of hexafluorides of 3*d* (CrF_6), 4*d* (MoF_6, TcF_6, RuF_6, RhF_6), 5*d* (WF_6, ReF_6, OsF_6, IrF_6, PtF_6), and 5*f* elements (UF_6, NpF_6, PuF_6). The vertical series of hexafluorides comprise (1) the hexafluorides of the non-metals in Group VI of the Periodic System (SF_6, SeF_6, TeF_6, PoF_6), (2) the hexafluorides of the transition elements of Group VI (CrF_6, MoF_6, WF_6, UF_6), (3) the hexafluorides of elements with one unshared electron (TcF_6, ReF_6, NpF_6), (4) the hexafluorides of elements with two unshared electrons (RuF_6, OsF_6, PuF_6), (5) the hexafluorides of elements with three unshared electrons (RhF_6, IrF_6), and (6) platinum hexafluoride (PtF_6). The platinum atom in this molecule has four unshared electrons which, judging from the type of the ground state of the PtF_6 molecule (Table 1), are paired. Xenon hexafluoride, the molecule of which does not belong to the symmetry point group O_h, occupies a special place.

The electronic ground states of eleven hexafluorides of sulphur, selenium, tellurium, molybdenum, tungsten, uranium, neptunium, plutonium, rhodium, iridium, and platinum are either non-degenerate or the degeneracy is predominantly of the spin type. The normal vibrational spectra of these molecules correspond to O_h symmetry. The vibrational spectra of the hexafluorides of technetium, ruthenium, rhenium, and osmium have appreciable anomalies (compared with the preceding hexafluorides), which are attributed to the dynamic Jahn–Teller effect[4,12-15]. According to the Jahn–Teller theorem[16], the orbital degeneracy of the electronic ground state of octahedral molecules is reduced by distortion of their configuration, i.e. by a decrease of molecular symmetry. This is the so called static Jahn–Teller effect. However, in the present case the static Jahn–Teller effect is not observed, but there is an anomaly in the infrared absorption spectra owing to a vibronic interaction.

Table 2. Width of the half-absorption bands of certain hexafluorides (cm^{-1}) [4].

Molecule	$\nu_{1/2}$		$\Delta\nu_{1/2}$	Molecule	$\nu_{1/2}$		$\Delta\nu_{1/2}$
	$\nu_1+\nu_3$	$\nu_2+\nu_3$			$\nu_1+\nu_3$	$\nu_2+\nu_3$	
MoF_6	20	31	0	WF_6	17	24	0
TcF_6	23	113	84	ReF_6	36	68	43
RuF_6	21	—	—	OsF_6	23	84	59
RhF_6	19	27	0	IrF_6	18	26	0
				PtF_6	20	26	0
Mean*	21	29		Mean*	20	25	

* The band widths for "anomalous" hexafluorides were disregarded in the averages.

The infrared spectra of the "normal" hexafluorides usually have two characteristic bands corresponding to the compound frequencies $\nu_1 + \nu_3$ and $\nu_2 + \nu_3$ in the region of 1140–1710 cm^{-1} and having almost identical intensities and outlines (Table 2). For each hexafluoride, the long wavelength band corresponds to the compound frequency $\nu_2 + \nu_3$ and the short wavelength band to the frequency $\nu_1 + \nu_3$. However, whereas the outlines of the $\nu_1 + \nu_3$ bands are virtually identical for both "normal" and "anomalous" hexafluorides, those of the $\nu_2 + \nu_3$ bands for different types of hexafluorides are not the same, which is a qualitative criterion of the "anomaly" of the hexafluorides.

The relations between the observed frequencies and the number of unshared valence electrons in the molecules of the "normal" hexafluorides, derived by Weinstock and Goodman[3,4], make it possible to estimate the vibration frequencies ν_2 and ν_5 which the molecules of the hexafluorides of technetium, ruthenium, rhenium, and osmium would have in the absence of the dynamic Jahn–Teller effect. The points corresponding to the ν_2 and ν_5 frequencies of the "anomalous" hexafluorides deviate from the graphical relations. It is interesting to note that the anomalies in the vibrational spectra of the hexafluorides of 4*d* and 5*d* elements are not repeated in the series of the hexafluorides of 5*f* elements.

III. RELATION BETWEEN THE VARIATION OF THE FORCE CONSTANTS OF HEXAFLUORIDES AND THEIR THERMAL STABILITIES AND REACTIVITIES

In certain reviews (for example those of O'Donnel and Stewart[5,6]) attempts are made to relate the regularities in the variation of the reactivities of hexafluorides in the first vertical series (CrF_6, MoF_6, WF_6, UF_6) to the valence force constants (f_d in Wilson's terminology[17]) and average energies of the E – F bonds. Several comments of

a general nature must be made concerning the estimation of the reactivities of hexafluorides with the aid of the force constants. The force constant† $f_d = (\partial^2 V/\partial q^2)_{q \to 0}$, where V is the potential energy of the molecule and q the vibrational coordinate, characterises the resistance of the molecule to the deformation of the equilibrium configuration. However, even for diatomic molecules there is no unambiguous relation between the force constant and the dissociation energy[18]. The quantity $(\partial^2 V/\partial q^2)_{q \to 0}$ characterises merely the curvature of the potential well in the vicinity of the equilibrium position but does not necessarily indicate its depth[19].

The multiplicity of models proposed for the description of the force field of a polyatomic molecule is due to the existence of a set of elastic structural elements the number of which is greater than the number of chemical bonds and independent nuclear coordinates. However, regardless of the choice of model, none of the different types of coefficients can provide a simple individual characteristic of a bond in a polyatomic molecule[20]. The extension of one bond involves a whole group of structural elements, since the valence force constant f_d depends not only on the interaction between two atoms but also on their interaction with other structural elements of the molecule. Only a set of force constants characterises an individual bond in a polyatomic molecule[21].

We shall consider to what extent various force constants of hexafluoride molecules can characterise their thermal stability and reactivity. In the present paper we shall employ the terminology adopted by Claassen[22]:

(1) f_d—valence force constant;
(2) f_α—deformation force constant for the bond angle;

Interaction Constants

(3) f_{dd}—for the interaction of bonds at right angles to one another;
(4) $f_{\alpha\alpha}$—for the interaction of adjacent angles in the same plane;
(5) $f_{d\alpha}$—for the interaction of an angle with the bonds forming its sides;
(6) δ—for the interaction of two opposite bonds;
(7) γ—for the interaction of an angle with a bond perpendicular to its plane;
(8) k—for the interaction between two angles in perpendicular planes having a bond in common;
(9) ϵ—for the interaction between two angles in perpendicular planes without a bond in common.

Seven independent force constants may be isolated for hexafluoride molecules[4]:

(1) $A = f_d$;
(2) $B = \delta$;
(3) $C = 2f_{dd}$;
(4) $D = 2(f_{d\alpha} - \delta)$;
(5) $E = f_\alpha - \gamma$;
(6) $F = 2(f_{\alpha\alpha} - \gamma)$;
(7) $G = 2(k - \epsilon)$.

Many investigators[4,22-36] analysed the normal vibrations of octahedral hexafluoride molecules and calculated the force constants. The force constants depend on the choice of model for the force field. In the present study only the force constants quoted in the review of Weinstock and Goodman[4] are considered. They are listed in Table 3.

† For diatomic molecules.

Figs. 1 and 2 present a graphical interpretation of the relation between the force constants of EF_6 molecules and the charge number of the element E (see p. 157).

Analysis of these relations permits the following conclusions: (1) the valence force constant exceeds approximately by two powers of ten all the remaining force constants; this is a general rule[37]; (2) the independent force constants A, B, E, and partly G of hexafluoride molecules increase on going from 4*d* to 5*d* elements and sharply decrease on going to 5*f* elements; (3) the force constants C and F also increase on going from 4*d* to 5*d* elements; on going to 5*f* elements, the constant C increases and the constant F changes in different ways for each of the vertical series; (4) the constant D decreases on moving downwards along the vertical series; (5) the constants A, B, C, and partly G decrease sharply on moving along the series of 4*d*, 5*d*, and 5*f* elements from left to right, which is consistent with the variation of the thermal stabilities of the hexafluorides; (6) the constants D, E, and F increase along the series of 4*d*, 5*d*, and 5*f* elements (from left to right).

Table 3. Force constants of octahedral hexafluoride molecules[4] [$cm^{-1}/(0.01\ Å)^2$].

Force constant	SF_6	SeF_6	MoF_6	TeF_6	RuF_6	RhF_6	TeF_6	WF_6
A	28.163	25.663	24.673	24.483	23.304	21.770	26.032	26.480
B	−1.125	0.666	1.673	0.860	0.331	−0.654	0.773	2.246
C	3.580	1.232	2.597	1.888	1.268	0.986	0.711	0.709
D	5.634	2.160	0.713	0.720	0.767	0.806	0.499	0.488
E	4.346	2.648	0.843	1.083	1.199	1.260	1.090	0.970
F	0.443	0.316	−0.555	−0.183	0.050	0.221	−0.317	−0.455
G	0.848	0.676	−0.415	0.214	0.205	0.234	−0.002	0.454

	ReF_6	OsF_6	IrF_6	PtF_6	UF_6	NpF_6	PuF_6
A	26.353	26.185	25.181	23.033	19.412	19.029	18.451
B	1.802	1.190	0.209	−1.033	0.066	−0.314	−0.425
C	2.293	1.744	1.418	1.322	3.038	2.702	2.314
D	0.480	0.531	0.543	0.526	0.210	0.244	0.255
E	1.243	1.400	1.432	1.446	0.663	0.832	0.899
F	−0.006	0.307	0.476	0.605	0.083	0.229	0.255
G	0.173	0.194	0.213	0.168	0.100	0.050	0.035

One may conclude that the variation of the majority of force constants along the horizontal and vertical series of hexafluorides is of the same type as that of the valence force constant f_d (A). The force constants for sulphur, selenium, and tellurium hexafluorides are quoted only for comparison.

Analysis of the feasible configurations of the xenon hexafluoride molecule[38] showed that it cannot have the structure of a regular octahedron. A model close to the structure of iodine heptafluoride, in which the missing bond is replaced by the electron pair of xenon, is more likely. This is confirmed both by the analysis of the infrared spectrum of xenon hexafluoride[39] and by the study of its structure by electron diffraction[40,41]. Therefore the force constants of XeF_6 cannot be compared with those of other hexafluorides.

On the hypothesis of a relation between the force constants, thermal stabilities, and reactivities of EF_6 molecules, the latter can be arranged in the following series in terms of their thermal stability:

Vertical series:

$$SF_6 > TeF_6 > SeF_6;$$
$$WF_6 > MoF_6 > UF_6;$$
$$ReF_6 > TcF_6 > NpF_6;$$
$$OsF_6 > RuF_6 > PuF_6;$$
$$IrF_6 > RhF_6.$$

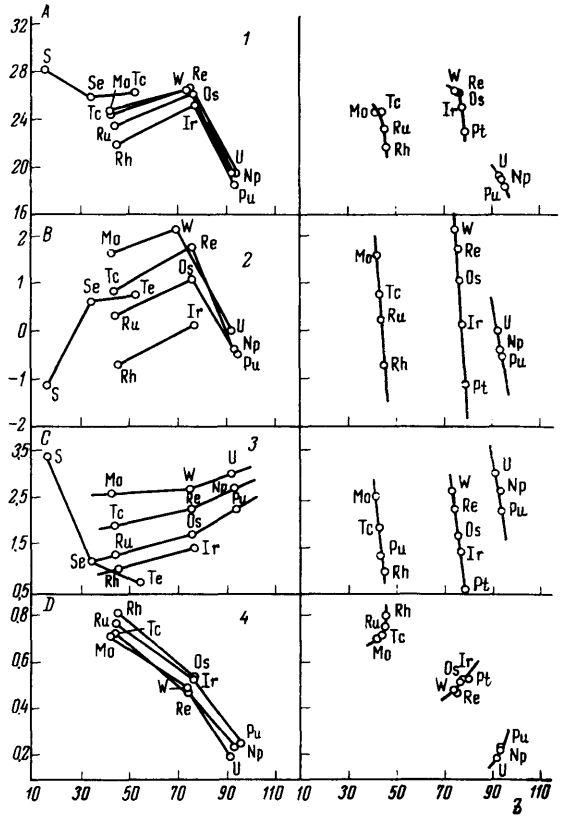

Figure 1. Variation of the force constants A, B, C, and D of EF_6 molecules with the charge number of the central atom of the element E in the vertical and horizontal series of hexafluorides.

Horizontal series:

$$MoF > TcF_6 > RuF_6 > RhF_6;$$
$$WF_6 > ReF_6 > OsF_6 > IrF_6 > PtF_6;$$
$$UF_6 > NpF_6 > PuF_6.$$

When all the elements are arranged in a single series, the following sequence is obtained:

$$SF_6 > WF_6 > ReF_6 > OsF_6 > TeF_6 > SeF_6 > IrF_6 > MoF_6 > TcF_6 > RuF_6 > PtF_6 > RhF_6 > UF_6 > NpF_6 > PuF_6.$$

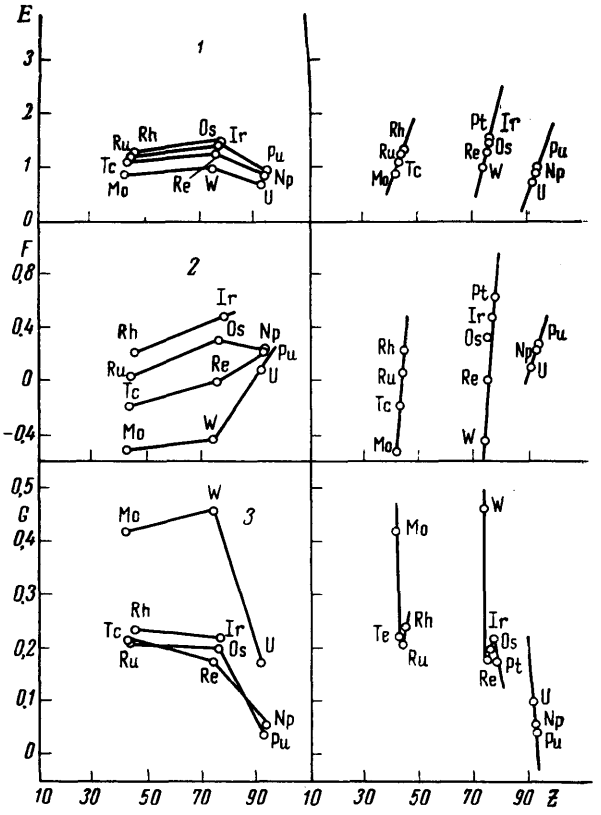

Figure 2. Variation of the force constants E, F, and G of EF_6 molecules with the charge number of the element E in the vertical and horizontal series of hexafluorides.

The last series probably does not fully reflect the actual relation between the thermal stabilities and reactivities of the hexafluorides. Therefore, before dealing with a comparative analysis of the experimental data, it is necessary to analyse the above relations by other methods.

IV. VARIATION OF THE AVERAGE BOND ENERGIES OF HEXAFLUORIDES IN HORIZONTAL AND VERTICAL SERIES

The average bond energy E_0 of the EF_n molecule is defined by the formula

$$E_0 = \frac{D_0^0}{n}, \qquad (1)$$

where D_0^0 is the heat of atomisation of the molecule and n is the number of bonds. The values of D_0^0 are not known for all hexafluorides and the accuracy of the calculation or estimation of some of them is low. For example, one may mention the discrepancy between the data of different workers for the heat of formation of gaseous plutonium hexafluoride: −460 kcal mole^{-1},[42] −473 kcal mole^{-1},[43] −411.2 kcal mole^{-1},[44] and −418 ± 8 kcal mole^{-1} [45]. The last value was recommended by Rand[45] as the most accurate.

The bond energies and heats of atomisation of certain hexafluorides are listed in Table 4. For the majority of the known hexafluorides, the heats of formation are known only under standard conditions, i.e. only the values of $\Delta H^{\circ}_{f,298}$ are available, and in order to find D^0_0 ($-\Delta H^0_0$) a correction must be calculated from the equation

$$\left[\frac{\partial(\Delta H^{\circ}_T)}{\partial T}\right]_p = \Delta C_p, \qquad (2)$$

where ΔC_p is the heat capacity change from 0° to 298°K.

Table 4. Heats of formation, heats of atomisation, and bond lengths and energies in hexafluoride molecules.

Hexafluoride	Heat of formation of hexafluoride from elements under standard conditions $\Delta H^{\circ}_{f,298}$, kcal mole^{-1}	References	Heat of atomisation of hexafluoride under standard conditions $-D^{\circ}_{298}$, kcal mole^{-1}	References	Heat of atomisation of hexafluoride at absolute zero D^0_0, kcal mole^{-1}*	References	Bond dissociation energy E^0_0, kcal	References	E–F bond length, Å	References
SF_6	−291.7	46	478.93	51	474.6	55	79.0		1.564±0.01	57
SeF_6	−266.9	46	439.2	51	434.9	56	72.5		1.688±0.010	57
TeF_6	−327.2	46	487.7	51	483.2		80.6		1.84±0.03	58
MoF_6	−382	47	653.5	51.52	649.2	55	108.2		1.83	60
TcF_6	−300	42	569	51.52	565		94.2		1.8512	56
RuF_6	—	—	—	—	—		—		1.8775	60
RhF_6	—	—	—	—	—		—		1.8738	60
WF_6	−411.5	48	729	51.53	725	55	120.9		1.833	59
ReF_6	−278	42	577	49.51	573		~95.5		—	
OsF_6	−225	42	526	51.52	522		~86.9		1.83	22
IrF_6	−130	42	403.8	51.52	399.5	55	66.55		1.833	22
PtF_6	—	—			—		—			
UF_6	−510.5	49	740.5	54	735.96	55	122.64		1.994	22
NpF_6	−461	42	680	51.52	675.6	55	112.8		1.980	22
PuF_6	−418	45	624	51.52	619.5	55	103.21		1.972	22
XeF_6	−82.9 kcal at 393° K	50					32.3	50	1.90	38

* Estimated from Eqn. (2).

The accuracy of the determination of ΔH°_{298} is usually not sufficiently high to make this correction, but nevertheless in the present study the correction was introduced.

Analysis of the results in Table 4 shows that the bond energies decrease in the horizontal series from left to right like the valence force constants (A) and the constant B, C, and partly G (see curves *1–3* in Fig. 1 and curve *3* in Fig. 2). In the vertical series the bond energy increases in the series of hexafluorides of 4*d*, 5*d*, and 5*f* elements. In the series of hexafluorides of sulphur, selenium, and tellurium, the E – F bond energy is 79.0, 72.5, and 80.6 kcal mole^{-1} respectively. The Xe–F bond has the lowest dissociation energy (only 32.3 kcal mole^{-1}).

Thus if it is supposed that the average bond energy characterises the thermal stability and reactivity of hexafluoride molecules (as was done by O'Donnel and Stewart[5]), then hexafluorides can be arranged in the following series in terms of decreasing thermal stability:

$$UF_6 > WF_6 > NpF_6 > MoF_6 > PuF_6 > ReF_6 > TcF_6 > OsF_6 > TeF_6 > SF_6 > SeF_6 > IrF_6 > XeF_6 .$$

The discrepancy between this series and the experimental stabilities and activities of hexafluorides will be discussed below.

V. INTERATOMIC DISTANCES AND BOND STRENGTH

The use of interatomic E–F distances to characterise the chemical properties of hexafluorides (Table 4) appears to be of doubtful value. In the series of hexafluorides of uranium, neptunium, and plutonium, the interatomic E–F distances decrease but in the series of hexafluorides of 4*d* and 5*d* elements it is difficult to establish a similar sequence. Probably Badger's equation[61], whereby the E–F bond lengths were found (see, for example, Ref. 56 and 60), does not ensure the necessary accuracy owing to the dependence of the calculated force constants on the force field model.

VI. ANALYSIS OF THE THERMODYNAMIC STABILITIES OF HEXAFLUORIDES

A rigorous characteristic of the dissociation of any chemical compound is its thermodynamic stability in this reaction. The thermodynamic stability is characterised by the reciprocal of the equilibrium constants K_e for the corresponding dissociation process:

$$\alpha = \frac{1}{K_e} = \exp\left(\frac{\Delta H^0_0}{RT} - \frac{\Delta \Phi^*_T}{R}\right), \qquad (3)$$

where $\Delta\Phi^*_T$ is the reduced free energy of the dissociation reaction, R the gas constant, and T the absolute temperature. The values of $K_e(\alpha)$ may be related to the corresponding yields of the dissociation products of hexafluorides. For example, for the reaction

$$(EF_6)_{gas} \rightarrow (E)_{gas} + 6(F)_{gas}, \qquad (4)$$

$$\alpha = \frac{(1-x)(1+6x)}{4.6656 \cdot 10^4 x^7 p^6}, \qquad (5)$$

where p is the pressure and x the number of moles of hexafluoride which have reacted.

The values of α depend both on the enthalpy change (ΔH^0_0) and on the change in the reduced free energy ($\Delta\Phi^*_T$), which are calculated from energy and geometrical molecular constants.

The thermodynamic functions for gases consisting of polyatomic molecules (including EF_6 molecules) are calculated in many cases in terms of the rigid rotator—harmonic oscillator approximation. The components of the thermodynamic functions due to translational, rotational, and vibrational motion are calculated. This is because the electronic ground states of polyatomic molecules are as a rule of the singlet type and therefore the partition function with respect to the intramolecular motion of the polyatomic molecule is equal to the sum of the vibrational and rotational partition functions of the electronic ground state[17]. The thermodynamic functions obtained are called virtual, since they do not include the components due to nuclear spins and the mixing of isotopes.

The multiplicity of the electronic ground state is taken into account by introducing into the thermodynamic functions the term $R \ln p_M$, where p_M is the statistical weight of this state.

It is assumed[17] that the electronic ground state of polyatomic molecules with an even number of electrons is of the singlet type (the statistical weight of the state is unity); electronic states with one free electron have a statistical weight of two. Some workers have calculated the thermodynamic properties of many hexafluorides in

terms of the approximation of the rigid rotator–harmonic oscillator model. The entropies, reduced free energies, heat capacities, and enthalpy changes have been calculated in the range 50–1600°K at $p = 1$ atm. for the hexafluorides of uranium[55], plutonium[55,62], molybdenum, tungsten, iridium, and neptunium[55] and in the range 50–2000°K for the hexafluorides of ruthenium, rhodium[60], and technetium[56]. It should be noted that some of the molecular constants employed by Nagarajan to calculate the thermodynamic functions of the above hexafluorides were subsequently revised by Weinstock and Goodman[4] (Table 5).

Table 5. Fundamental vibration frequencies of hexafluoride molecules.

Molecule*	ν_1 (1)	ν_2 (2)	ν_3 (3)	ν_4 (3)	ν_5 (3)	ν_6 (3)
SF_6	770	640	639	614	522	349
SeF_6	708	(661)	780	437	(403)	(262)
TeF_6	701	674	752	325	313	(195)
PoF_6	[700]	[682]	[741]	[253]	[243]	[144]
MoF_6	741	643	741	262	(312)	(122)
TcF_6	(712)	(639)**	748	265	(257)**	[174]
RuF_6	(675)	(624)**	735	275	(283)**	[186]
RhF_6	(634)	(592)	724	283	269	(189)
PdF_6	[590]	[525]	[711]	[280]	[258]	[191]
WF_6	(771)	(673)	711	258	(315)	(134)
ReF_6	755	(671)**	715	257	(295)**	(193)
OsF_6	(733)	(668)**	720	272	(276)**	[205]
IrF_6	(701)	(646)**	719	276	(258)	(206)
PtF_6	655	(600)	705	273	(242)	[211]
UF_6	667	535	624	(184)	(201)	(140)
NpF_6	(648)	(528)	624	(198)	(205)	(165)
PuF_6	(628)	(523)	616	(203)	(211)	(173)
AmF_6	[609]	[500]	[603]	[205]	[216]	[178]
CrF_6	(720)	(650)	790	[266]	[309]	[110]

*The degree of degeneracy of the given vibration is indicated in brackets after ν_1, ν_2, etc.

** The estimate was made from the variation of the vibration frequencies with the number of free electrons in the hexafluoride molecules[4]; these are postulated frequencies in the absence of vibronic interaction. The frequencies obtained from the above relation and virtually identical with the experimental values are indicated in round brackets; the frequencies calculated from the Raman frequencies are indicated in square brackets.

The ν_6 frequencies for molybdenum and tungsten hexafluorides, the ν_2 frequency for technetium hexafluoride, etc. have been revised. The Mo–F bond length in the MoF_6 molecule, assumed by Nagarajan to be 1.56 Å,[63] is inconsistent with a later value of 1.83 Å.[59] Moreover, the statistical weight of the electronic ground state in the case of its degeneracy was not taken into account in any of the calculations. This applies to the hexafluorides of technetium, ruthenium, rhodium, rhenium, osmium, iridium, and neptunium.

According to Moffit et al.[64] the lower electronic states of the hexafluorides of rhenium and osmium are orbitally degenerate and the Jahn–Teller theorem predicts instability of the octahedral configuration. As already mentioned above, such instability does not lead to a static distortion of the symmetrical configuration in the gas phase. This is shown by the similarity of the electronic spectra of the hexafluorides of rhenium and osmium on the one hand and those of iridium and platinum on the other. For the last two hexafluorides, the Jahn–Teller theorem does not predict instability of the octahedral configuration. The number of electronic bands in the spectra of all four hexafluorides corresponds to the number predicted by the ligand field theory for the configuration with the O_h symmetry; the absence of the static distortion of the EF_6 molecules was demonstrated by electron diffraction[4] and by the analysis of the infrared spectra of the "anomalous" hexafluorides. In the case of static distortion, one might expect that the force constants for the longer bonds (or larger angles) would differ from the force constants for the shorter bonds (or smaller angles); moreover, one might observe splitting of the infrared absorption bands. The analogies in the vibrational spectra have been interpreted on the basis of a vibronic interaction[12,65]. Quantitatively this interaction was investigated by Weinstock and coworkers[4,14,15,66].

Table 6. Effect of vibronic interaction on the thermodynamic properties of hexafluorides[4].

Hexafluoride	T, °K	$\Delta\Phi^*_T$, cal mole^{-1} deg^{-1}	$\Delta(H^0_T - H^0_0)$, cal mole^{-1}	ΔS^0_T, cal mole^{-1} deg^{-1}
ReF_6	200	0.103	18.5	0.196
	298.15	0.136	20.2	0.203
	900	0.175	12.4	0.189
TcF_6	200	0.087	17.1	0.172
	298.15	0.117	19.1	0.181
	900	0.154	11.1	0.166

The empirical relations between the ground vibration frequencies and the number of unbound electrons[4] enabled Weinstock and Goodman to estimate the frequencies of the hitherto not investigated (CrF_6, PoF_6) and not even synthesised (AmF_6) hexafluorides. The effect of the vibronic interaction on the thermodynamic properties was also estimated by Weinstock and Goodman[4] (Table 6). The corrections obtained ($\Delta\Phi^*_T$ and ΔS^0_T) are virtually negligible for TcF_6 and ReF_6 in the range 200–900°K. Such an error in the calculations of the thermodynamic functions is possible as a result of an error of 1–2 cm^{-1} in the estimation of the vibration frequencies.

For the hexafluorides of osmium and ruthenium, the corrections are of the same order of magnitude as those for ReF_6 and TcF_6, which are listed in Table 6. This implies that the ν_2 and ν_5 frequencies (Table 5) may be employed without additional correction to calculate the thermodynamic properties of rhenium, technetium, ruthenium, and osmium hexafluorides.

Table 7 lists the reduced free energies of certain hexafluorides required for the calculation of their thermodynamic stabilities. They were calculated in terms of the rigid rotator–harmonic oscillator approximation taking into account the corrections for frequencies in the review of Weinstock and Goodman[4] and for the degeneracy of the electronic ground state.

The reduced free energies of the elements forming hexafluorides were taken from Kulikov's monograph[52] and the paper of Gurvitsh and Jungman[67]. The thermodynamic stability constants of the hexafluorides of certain elements were calculated by Eqn. (3) (Table 8).

Fig. 3 presents the logarithms of the thermodynamic stability constants of the hexafluorides in the vertical series at 298°, 1200°, and 2400°K. Analysis of these relations permits the following conclusions:

1. The thermodynamic stabilities of hexafluorides in relation to atomisation reactions decrease along the horizontal series (4*d*, 5*d*, and 5*f* elements).

Table 7. Reduced free energies of certain hexafluorides (cal mole^{-1} deg^{-1}) at p = 1 atm. in the ideal gas state.

T, °K	SF_6	SeF_6	TeF_6	MoF_6	TcF_6	WF_6	ReF_6	OsF_6	IrF_6	UF_6	NpF_6	PuF_6
298	56.64	59.06	62.42	64.46	65.90	65.11	66.63	66.93	66.68	68.74	69.48	67.36
400	62.01	64.21	68.13	70.52	71.83	71.16	72.56	72.84	72.65	75.44	76.08	73.93
800	74.88	80.07	85.06	88.10	89.30	88.67	89.89	90.13	90.06	94.26	94.73	92.54
1200	85.21	91.46	96.88	100.17	101.82	100.71	101.87	102.10	102.08	106.85	107.26	105.06
1600	93.38	100.27	105.91	109.32	110.47	109.86	110.99	111.22	111.23	116.30	116.67	114.48
2000	100.11	107.43	113.22	116.72	117.84	117.23	118.34	118.57	118.60	123.86	124.22	122.02
2400	105.84	113.46	119.34	122.85	124.01	123.40	124.50	124.73	124.77	130.15	130.50	128.30
2800	110.82	118.67	124.61	128.19	129.32	128.71	129.80	130.03	130.07	135.55	135.89	133.69
3200	115.21	123.24	129.24	132.84	133.37	133.36	134.45	134.67	134.73	140.28	140.61	138.41
3600	119.16	127.33	133.36	136.99	138.10	137.51	138.15	138.75	138.85	144.37	144.82	142.62
4000	122.72	131.01	137.08	140.73	141.85	141.25	141.90	142.43	142.60	148.15	148.58	146.38

Table 8. Thermodynamic stability constants of hexafluorides

T°, K	SF_6	SeF_6	TeF_6	MoF_6	TcF_6	WF_6	ReF_6	OsF_6	IrF_6	UF_6	NpF_6	PuF_6
1200	$2.24\cdot10^{41}$	$1.12\cdot10^{42}$	10^{46}	$3.17\cdot10^{27}$	$1.45\cdot10^{60}$	$4\cdot10^{91}$	$5.62\cdot10^{51}$	$5.62\cdot10^{51}$	$1.91\cdot10^{30}$	$4.47\cdot10^{93}$	$1.59\cdot10^{83}$	$1.7\cdot10^{73}$
1600	$6.32\cdot10^{19}$	$4.47\cdot10^{34}$	$5.61\cdot10^{28}$	$5.38\cdot10^{47}$	$5\cdot10^{84}$	$1.78\cdot10^{55}$	$7.93\cdot10^{35}$	$1.26\cdot10^{28}$	$1.59\cdot10^{12}$	$6.31\cdot10^{59}$	$2\cdot10^{52}$	$7.94\cdot10^{42}$
2000	$8.69\cdot10^{6}$	$5.13\cdot10^{3}$	$4.17\cdot10^{10}$	$7.88\cdot10^{29}$	$3.17\cdot10^{19}$	$2\cdot10^{38}$	$1.26\cdot10^{20}$	$1.15\cdot10^{14}$	$1.74\cdot10^{1}$	$7.95\cdot10^{39}$	$7.93\cdot10^{33}$	$7.94\cdot10^{27}$
2400	$1.8\cdot10^{-2}$	$6.45\cdot10^{-5}$	$6.38\ 10^{1}$	$9.13\cdot10^{17}$	$1.66\cdot10^{9}$	$1.6\cdot10^{27}$	10^{10}	$4.17\cdot10^{4}$	$1.23\cdot10^{-6}$	$1.59\cdot10^{26}$	$2.3\cdot10^{21}$	$1.5\cdot10^{15}$
2800	$1.48\cdot10^{-8}$	$1.48\cdot10^{-10}$	$3.72\ 10^{-5}$	$4.21\cdot10^{9}$	$9.6\cdot10^{1}$	$1.74\cdot10^{17}$	$3.39\cdot10^{2}$	$8.84\cdot10^{-3}$	$1.2\cdot10^{-12}$	$2.82\cdot10^{14}$	$3.8\cdot10^{12}$	$9.5\cdot10^{8}$
3200	$3.02\cdot10^{-13}$	$4.67\cdot10^{-15}$	$6.03\cdot10^{-10}$	$1.63\cdot10^{3}$	$2.35\cdot10^{-4}$	$1.34\cdot10^{8}$	$1.13\cdot10^{-3}$	$6.17\cdot10^{-8}$	$1.82\cdot10^{-15}$	$2.37\cdot10^{9}$	$5.94\cdot10^{5}$	$9\cdot10^{1}$
3600	$7.07\cdot10^{-17}$	$5.49\cdot10^{-18}$	$1.42\cdot10^{-13}$	$1.91\cdot10^{-2}$	$1.48\cdot10^{-6}$	$4.46\cdot10^{2}$	$4.22\cdot10^{-8}$	$8.5\cdot10^{-11}$	$3.98\cdot10^{-19}$	$6.02\cdot10^{3}$	2.82	$1.55\cdot10^{-3}$
4000	$1.2\cdot10^{-19}$	$1.55\cdot10^{-20}$	$2.83\cdot10^{-17}$	$2.69\cdot10^{-1}$	$7.1\cdot10^{-10}$	$1.94\cdot10^{-2}$	$1.29\cdot10^{-11}$	$7.24\cdot10^{-15}$	$8.9\cdot10^{-21}$	$2.56\cdot10^{-1}$	$1.44\cdot10^{-5}$	$6.68\cdot10^{-8}$

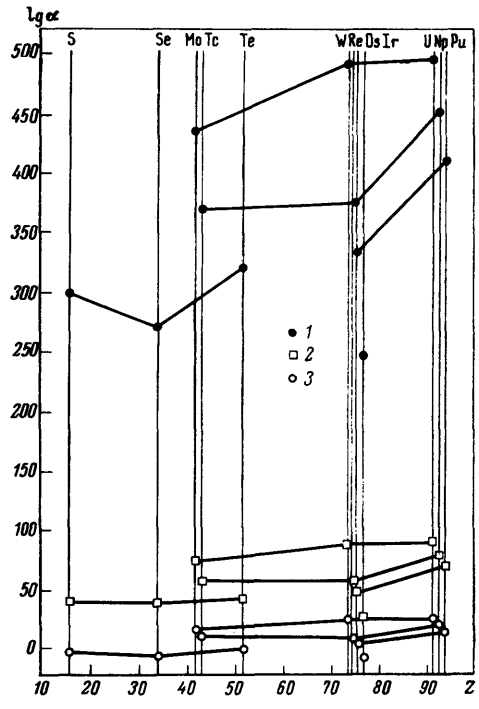

Figure 3. Variation of the logarithms of the thermal stability constants of hexafluorides with the charge number of the central atom; temperature (°K): 1) 298; 2) 1200; 3) 2400.

2. The sequence of hexafluorides in terms of decreasing thermodynamic stability depends little on temperature. In the vertical series the hexafluorides of the actinide elements are the most stable:

$$UF_6 > WF_6 > MoF_6;\ NpF_6 > ReF_6 > TcF_6;\ PuF_6 > OsF_6.$$

However, the difference between the values of $\lg \alpha$ diminishes as the temperature is raised, owing to an increase of the contribution by the entropy factor to the equation $\Delta G = \Delta H - T\Delta S$ compared with the heat of reaction.

3. In the series of non-metal hexafluorides the stability falls from sulphur hexafluoride to selenium hexafluoride, but increases sharply on going to tellurium hexafluoride, so that $TeF_6 > SF_6 > SeF_6$.

4. The sequence of hexafluorides in terms of decreasing thermodynamic stability in relation to the atomisation reaction is as follows:

$$UF_6 > WF_6 > NpF_6 > MoF_6 > PuF_6 > TcF_6 > ReF_6 > OsF_6 > TeF_6 > SF_6 > SeF_6 > IrF_6.$$

The positions of the hexafluorides in this series depend to a considerable degree on the accuracy of the determination of ΔH_0^0 (Table 9). Xenon hexafluoride should occupy the last place in this series.

We shall examine the changes in the thermodynamic stability of hexafluorides in partial dissociation reactions in the first vertical and third horizontal series. The decomposition to the tetrafluoride may be employed as a reaction of this kind:

$$(EF_6)_{gas} \rightarrow (EF_4)_{gas} + 2(F)_{gas}. \qquad (6)$$

The reduced free energies of the tetrafluorides required for the calculation of the stability constants were evaluated

in terms of the rigid rotator–harmonic oscillator model using an empirical method for the estimation of the equivalent geometrical and energy constants[68]. The results of the calculation are presented in Table 10. The calculation was made for only six hexafluorides, since only in these cases was it possible to calculate the heats of reaction at the standard temperature (298.16°K) and the absolute zero (Table 9).

Table 9. Enthalpies of dissociation of hexafluorides by reaction (6) under standard conditions (298.16°K) and at the absolute zero (kcal mole^{-1}).

Hexafluoride	ΔH°_{298}	ΔH°	References to literature employed in calculations	Hexafluoride	ΔH°_{298}	ΔH°	References to literature employed in calculations
UF_6	184.4	181.4	49,69,70	WF_6	234	232	42.48
NpF_6	131	129	42,71	MoF_6	194	191	42.47
PuF_6	102.5	101.3	45	SF_6	—	152,261	17

Table 10. Thermodynamic stability constants of hexafluorides in reaction (6).

T°, K	UF_6	NpF_6	PuF_6	WF_6	MoF_6	SF_6
800	10^{35}	$1.32\cdot10^{21}$	$2.24\cdot10^{13}$	$1.78\cdot10^{48}$	$7.93\cdot10^{27}$	$4.36\cdot10^{28}$
1200	$1.12\cdot10^{17}$	$1.12\cdot10^{9}$	$4.8\cdot10^{3}$	$5.38\cdot10^{23}$	$1.13\cdot10^{20}$	$2.1\cdot10^{14}$
1600	$1.2\cdot10^{9}$	$1.23\cdot10^{3}$	$1.04\cdot10^{-1}$	$1.27\cdot10^{16}$	$1.76\cdot10^{11}$	$1.48\cdot10^{4}$
2000	$2.76\cdot10^{4}$	$1.34\cdot10^{-1}$	$1.78\cdot10^{-4}$	$5.49\cdot10^{9}$	$7.24\cdot10^{5}$	$8.9\cdot10^{-1}$
2400	$1.66\cdot10^{1}$	$1.37\cdot10^{-3}$	$2.29\cdot10^{-6}$	$3.03\cdot10^{5}$	$2.21\cdot10^{2}$	$1.23\cdot10^{-3}$
2800	$8.92\cdot10^{-1}$	$2.81\cdot10^{-5}$	$1.1\cdot10^{-7}$	$2.95\cdot10^{2}$	$6.88\cdot10^{0}$	$2.2\cdot10^{-5}$
3200	$1.74\cdot10^{-3}$	$1.62\cdot10^{-6}$	$1.15\cdot10^{-8}$	$1.61\cdot10^{0}$	9.10^{-3}	$3.81\cdot10^{-7}$

The logarithms of the thermodynamic stability constants of the hexafluorides decrease from left to right along the series of 5*f* elements. When the hexafluorides are arranged in a common series in terms of decreasing thermal stability with respect to reaction (6), the following sequence is observed up to 2300°K: $WF_6 > MoF_6 > UF_6 > SF_6 > NpF_6 > PuF_6$. Above 2300°K, SF_6 and NpF_6 change places.

VII. ANALYSIS OF EXPERIMENTAL DATA FOR THE THERMAL STABILITIES AND REACTIVITIES OF HEXAFLUORIDES

The chemical reactivities‡ of non-metal hexafluorides differ markedly from those of metal hexafluorides. With the exception of polonium hexafluoride, non-metal hexafluorides exhibit unusual chemical inertness. In the reviews by Weinstock already mentioned[2,3], it is reported that the thermal stabilities in this series decrease and the chemical reactivities increase from sulphur hexafluoride to tellurium hexafluoride, the hydrolysis of tellurium hexafluoride, which is the most reactive of the three hexafluorides, requiring not less than 24 h for its completion at room temperature[3]. The information available at present about the thermal stability of sulphur hexafluoride is fairly adequate. The compound is stable in an electric arc[72], which can be accounted for[3] by its high thermal stability. At 2300–2500°K sulphur hexafluoride molecules dissociate into atoms[46]. A wide variety of fragments of SF_6 molecules, obtained in an electric arc, have been isolated[73,74]. The reason for the pronounced insulating properties of sulphur hexafluoride is probably the high electron affinity not only of fluorine atoms and molecules, but also of SF_6 molecules and their fragments[75].

We shall consider the experimental regularities in the variation of the thermal stability and reactivity in the vertical and horizontal series of metal hexafluorides. The first vertical series includes the hexafluorides of chromium (3*d*), molybdenum (4*d*), tungsten (5*d*), and uranium (5*f*). The molecules of all these hexafluorides do not have free electrons. Their chemical reactivity may be characterised by the reactions involving the fluorination of the lower fluorides of various elements (including the lower fluorides of the elements forming the hexafluorides), the sensitivity to hydrolysis, substitution and addition reactions, etc.

The feasibility of reaction (3) is a direct indication that tungsten hexafluoride is chemically less reactive than molybdenum hexafluoride:

$$(WF_4)_{solid} + 2(MoF_6)_{gas} \rightarrow 2(MoF_5)_{solid} + (WF_6)_{gas}. \quad (7)$$

Chromium hexafluoride is thermally unstable at −100°C.[76] Even chromium pentafluoride is more reactive than the hexafluorides of molybdenum, tungsten[11], and uranium[6]. This was demonstrated by studies of the reactions of the above fluorides with the trifluorides of phosphorus, arsenic, bismuth, etc. The reaction with carbon disulphide is particularly instructive:

$$CS_2 + 8CrF_5 \rightarrow 8CrF_3 + CF_4 + 2SF_6, \quad (8)$$

$$2CS_2 + 6MoF_6 \rightarrow (CF_3)_2S_2 + 2S + 6MoF_5. \quad (9)$$

Reaction (8) takes place explosively[11], reaction (9) is also vigorous[11], but tungsten hexafluoride does not react with carbon disulphide[11]. Uranium hexafluoride fluorinates carbon disulphide, various fluorination products being obtained, depending on temperature.[6,77]

On the basis of studies of the behaviour of these four hexafluorides, O'Donnel[6,7,11] believes that the reactivity of the hexafluorides in the first vertical series diminishes in the following sequence: $CrF_6 > UF_6 > MoF_6 > WF_6$. Thus the hexafluoride of uranium (a 5*f* element) is more reactive than the hexafluorides of molybdenum (4*d*) and tungsten (5*d*).

In the series of hexafluorides of 5*f* elements (uranium, neptunium, and plutonium), the reactivity increases from UF_6 to PuF_6.[2–4,6,71]. Uranium hexafluoride may be obtained by the fluorination of the tetrafluoride with plutonium hexafluoride[88]. Neptunium and plutonium hexafluorides are readily decomposed photochemically, so that it is impossible to record their Raman spectra. Americium hexafluoride, the existence of which may be postulated by analogy with platinum hexafluoride, is probably even more unstable[79].

The transition elements of the second intercalary decade (4*d* elements) form four hexafluorides: MoF_6, TcF_6, RuF_6, and RhF_6. Ruthenium and rhodium hexafluorides oxidise xenon even at room temperature, like platinum and plutonium hexafluoride[50], in contrast to UF_6, NpF_6, IrF_6, and OsF_6. Technetium hexafluoride is reduced more readily than rhenium hexafluoride[80]. The hexafluorides of technetium and ruthenium are thermally

‡ As in the work of Canterford and O'Donnel[7], it is assumed that the increase of the thermal stability of the molecule is accompanied by a decrease of its chemical reactivity.

and photochemically unstable, so that it is impossible to obtain their Raman spectra. Molybdenum hexafluoride is the most stable in this series, the other hexafluorides being probably thermally unstable. The experimental evidence for the increase of the reactivity of the hexafluorides from left to right in this series is inadequate, but it is postulated that rhodium hexafluoride is thermally less stable than ruthenium hexafluoride[81].

The series of hexafluorides of 5*d* elements contains WF_6, ReF_6, OsF_6, IrF_6, and PtF_6. Platinum hexafluoride fluorinates the fluorides of neptunium and plutonium to the corresponding hexafluorides[72]. Selenium tetrafluoride reduces platinum hexafluoride to the tetrafluoride, but the hexafluorides of osmium and iridium pass to the pentavalent state under the same conditions[82]. Tungsten hexafluoride does not react with nitric oxide[83], osmium hexafluoride forms $NO^+OsF_6^-$,[83] and iridium and platinum form $(NO)_2IrF_6$ [85] and $(NO)_2PtF_6$ [84] respectively. Canterford and O'Donnel arranged the hexafluorides of 5*d* elements in the following sequence in terms of decreasing thermal stability: $WF_6 > OsF_6 > IrF_6 > PtF_6$. In addition[7], $OsF_6 > RuF_6$, $IrF_6 > RhF_6$.

Among the least thermally stable metal hexafluorides of various series, plutonium hexafluoride has a higher thermal stability than platinum hexafluoride; neptunium and uranium hexafluorides are more stable than ruthenium, rhodium, and platinum hexafluorides. The least stable hexafluoride is probably that of chromium§. There is evidence that the thermal stability of rhodium hexafluoride is lower than that of platinum hexafluoride[85]. From this standpoint, the least stable metal hexafluorides can probably be arranged in the following series in terms of decreasing thermal stability: $PuF_6 > PtF_6 > RhF_6 > CrF_6$.

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Analysis of the results presented in this review leads to the conclusion that the thermal stability of a particular hexafluoride, as a characteristic of its reactivity, depends on the type of the dissociation reaction considered. Depending on whether the hexafluoride dissociates completely into atoms or only partially to the penta- or tetrafluoride, a particular sequence of hexafluorides in the vertical and horizontal series in terms of varying thermal stability is obtained.

The experimental thermal stability and reactivity series characterising the incomplete conversion of metal hexafluorides, mainly to the penta- or tetra-fluorides within the limits of individual groups, correspond to changes in the majority of the force constants.

However, if all the hexafluorides are arranged in a single sequence in terms of decreasing valence force constants, the latter is not consistent with the experimental thermal stability series.

The experimental data for non-metal hexafluorides do not agree fully with the variation of the force constants. Probably a higher force constant for the bond is a necessary but not sufficient condition for a higher thermal stability of the hexafluoride. The shifts occurring in the dissociation of the E – F bond are so large, even on partial dissociation, that they no longer depend on the force constants. Moreover, if stepwise dissociation of the E – F bond is postulated, then for reactions (6) one must consider not only the *fd* constant of the EF_6 molecule, but also the *fd* constant of the EF_5 molecule, since on transition from the hexafluoride to the pentafluoride both the geometrical configuration and the average bond energy of the molecule change. For example, the average energy of the U – F bond in the uranium hexafluoride molecule is 122.24 kcal and in the pentafluoride 137 kcal $mole^{-1}$.

The equilibrium constants for the dissociation of hexafluorides to the corresponding tetrafluorides [reaction (6)] probably constitute a more objective criterion of the stability of the hexafluoride in relation to incomplete dissociation (Table 10). In this case the thermal stability of the hexafluoride decreases in the following sequence:

$$WF_6 > MoF_6 > UF_6 > SF_6 > NpF_6 > PuF_6 > PtF_6 > RhF_6 > CrF_6 .$$

From this point of view, the great inertness of sulphur hexafluoride is to be accounted for not by thermodynamics but by kinetic characteristics. The reasons for the position of the hexafluorides SeF_6, TeF_6, TcF_6, OsF_6, IrF_6, and RuF_6 in this series are still not quite clear.

Probably the most objective characteristic of the stability of hexafluorides in relation to total dissociation (atomisation) is provided by the thermodynamic stability constants. The estimates of thermal stability from the average energies of the E – F bonds in hexafluoride molecules agree fully, except for rhenium hexafluoride, with the thermodynamic estimates. The valence force constants are altogether unsuitable to characterise the stability of hexafluorides in relation to the atomisation reaction. The discrepancy between the thermal stability and force constant series constitutes indirect evidence that the decomposition of hexafluorides to atoms takes place via stepwise abstraction of fluorine atoms and, instead of a single force constant of the bond, one must take into account all the force constants of the E – F bonds in the molecules of the hexa-, penta-, tetra-, tri-, di-, and mono-fluorides of the elements.

§ Only the hexafluorides having the octahedral configuration with the O_h symmetry are considered.

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Alkali and Alkaline Earth Metal Ozonides

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Data published in the Soviet and foreign literature on alkali and alkaline earth metal ozonides are described systematically and critically discussed. The methods of their preparation, physicochemical properties and reactivities have been examined. Certain concepts concerning the mechanism of the formation of ozonides have been presented.
The bibliography includes 87 references.

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I. GENERAL INFORMATION ABOUT ALKALI METAL OZONIDES

As early as the middle of the nineteenth century certain investigators[1,2] noted that alkali metal hydroxides react with ozone to form coloured products, the nature of which was not established. However, the studies in this field up to 1949 were largely qualitative.

Baeyer and Villiger[3] suggested that the coloured products of the reaction of ozone with KOH and RbOH are salts of the hypothetical ozonic acid H_2O_4. Bach[4] believed that the reaction of ozone with potassium hydroxide takes place according to the equation

$$KOH + O_3 \rightarrow KO_4H .$$

The first attempt to investigate the nature of ozonides was made in 1912. Traube[5] showed that the products of the reaction of ozone with potassium hydroxide contain, apart from the two higher potassium oxides K_2O_2 and K_2O_4 and the unreacted potassium hydroxide, a small amount of an orange substance. At room temperature the substance immediately decomposed to K_2O_4. Traube suggested that K_2O_4 is a product of the decomposition of a higher potassium oxide, which he called "ozonate".

In a later study Traube[6] attempted to determine the amount of oxygen evolved on decomposition of potassium "ozonate". He regarded potassium "ozonate" as a compound in which an oxygen molecule is joined by subsidiary valences to one or two KOH molecules, i.e. $KOH.O_2$ or $(KOH)_2.O_2$. According to Traube, these formulae emphasise the capacity of ozonides to evolve molecular oxygen on interaction with water. He represented the conversion of potassium ozonide into the tetroxide as a two-stage process: in the first stage "potassium ozonate" undergoes intramolecular oxidation according to the equation

$$2(KOH)_2 \cdot O_2 = 2K_2O_2 + 2H_2O + O_2 , \quad (1)$$

and in the second stage the potassium peroxide formed reacts with another "ozonate" molecule to produce potassium tetroxide and hydroxide:

$$K_2O_2 + (KOH)_2 \cdot O_2 = K_2O_2 \cdot O_2 + 2KOH . \quad (2)$$

To test the hypothesis that metal ozonides do not contain hydrogen, Strecker and Thienemann[7] investigated the reaction of ozone with pure metals dissolved in liquid ammonia. When ozone was introduced into the blue solution of potassium in liquid ammonia, a white mass was formed initially and then the blue colour disappeared and a dark-brown precipitate and a dark-orange solution were produced. According to the author's hypothesis, the precipitate contained an admixture of a compound of the metal with ozone. Precipitates with admixtures of sodium, rubidium, and caesium ozonides were obtained in this way. The stability of the precipitates decreased from caesium to sodium, as noted previously by Manschot and Kampschulte[8]. Strecker and Thienemann did not succeed in obtaining pure preparations of the "ozone compounds" and in determining accurately their composition because of the marked contamination of the reaction products by ammonium nitrate and nitrite. Therefore it was necessary to investigate the reaction of ozone with ammonia. Strecker and Thienemann[7] showed that nitrates and nitrites are formed in the reaction of ozone with liquid ammonia according to the following equations:

$$2NH_3 + 4O_3 \rightarrow (NH_4)NO_3 + 4O_2 + H_2O , \quad (3)$$

$$2NH_3 + 3O_2 \rightarrow (NH_4)NO_2 + 3O_2 + H_2O . \quad (4)$$

They observed[7] that, when ozone is passed through liquid ammonia, an intense orange colour appears in solution, and rapidly disappears when ammonia is evaporated. The same phenomenon was noted by Manschot and Kampschulte[8]. Strecker and Thienemann suggested that, as with alkalis, an unstable ammonia compound is formed in this system and is readily converted into ammonium nitrate and nitrite.

In 1927 Fichter and Bladergroen[9] published the results of studies in which "potassium ozonide" was obtained on passing fluorine through a concentrated potassium hydroxide solution at −20°C. The resulting preparations were coloured brown. Fichter and Bladergroen suggested that they obtained the same products as Baeyer and Villiger in the reaction of ozone with potassium hydroxide.

Thus in the studies published up to 1949, there was no unanimity concerning the composition of the ozonation products. The reason was that investigators were unable to isolate in a pure form and to elucidate the nature of the coloured substances obtained in the reaction of ozone with alkali metal hydroxides. These substances were called "ozonates" and compositions identical with

those of derivatives of the hypothetical ozonic acid in the form of normal-(K_2O_4) and acid (KHO_4) salts were attributed to them. Later these compounds were regarded as molecular compounds of oxygen with one or two molecules of alkali: $KOH...O_2$ or $(KOH)_2...O_2$.

The present interest in the chemistry of inorganic ozonides was aroused by the work of Kazarnovskii and coworkers[10-14], where the possibility of isolating alkali metal ozonides in a crystalline state was demonstrated for the first time. Crystalline KO_3 (purity about 91%) and very small amounts of NaO_3 (purity up to 90%) and RbO_3 and CsO_3 (purity up to 66%) were obtained.

II. MODERN CONCEPTS CONCERNING ALKALI METAL OZONIDES

A recent study of the physicochemical properties of alkali metal ozonides[10,15] showed that they are higher oxides $M^+O_3^-$ with the molecular ion O_3^-. The presence of the molecular ion O_3^- in ozonides was first established by magnetic[10] and X-ray diffraction[12,16] measurements and was confirmed by spectrophotometry[17,18] and electron spin resonance[17-21].

Two resonating structures with a single free valence were attributed to the O_3^- ion on the basis of magnetic data[10,22]. Measurements of magnetic susceptibility confirm this[10]. $\chi_g = +12.5 \times 10^{-6}$ was found at 20°C, whence $\chi(\text{corr}) = +13.6 \times 10^{-6}$; this gives $\mu = 1.76$ Bohr magnetons, which is close to the theoretical value 1.73 Bohr magnetons for a single unpaired electron.

According to Pauling's data[22], the O–O bond length is 1.35 Å and the <OOO angle between the oxygen atoms is 108°. Starting with the angular form of the O_3 molecule, with an angle of 116° ± 0.5° between the O–O–O bonds and an O–O distance $r = 1.278 \pm 0.002$ Å, Smith[23] found by extrapolation that, like ozone, the O_3^- ion is non linear and has an angle of 110° ± 5° and a distance r = 1.34 ± 0.05 Å, which agrees well with Pauling's data. X-Ray diffraction study[16] showed that the O_3^- ion has an angular configuration with <OOO = 100° and $r = 1.19$ Å, which agrees well with the data of Herman and Giguere[18], who determined the O–O bond length in the O_3^- ion as 1.22 Å on the basis of the infrared spectrum of ammonium ozonide. They also showed[18] that the O_3^- ion does not show a tendency towards dimerisation, in contrast with the isoelectronic NO_2^{2-} ion[24,25], and with the NO_2 molecule.

In an E.S.R. study of potassium ozonide specimens at room temperature and the temperature of liquid nitrogen, Piskunov et al.[19] confirmed the data of Bennet et al.[20] and Marshall and van Osterburg[21]. The closeness of the g-factor to two and also the occurrence of appreciable exchange interaction confirm the above hypothesis that the magnetism of the molecular ion O_3^-, which is responsible for the observed paramagnetic resonance in KO_3, is of the free radical type[19]. The O_3^- ion, which has an odd number of electrons, is the carrier of the enormous chemical reactivity of ozonides, which may be regarded as unusually longlived free radicals. Measurements of the g-factor for perpendicular and parallel orientations of KO_3 gave $g_\perp = 2.012 \pm 0.002$ and $g_\parallel = 2.005 \pm 0.003$.

Nikol'skii et al. estimated the heat of formation of alkali metal ozonides[11] from the known heats of formation of KO_3 (−62.1 kcal mole^{-1}) [14] and an estimate of the lattice energy. Table 1 lists the heats of formation of alkali metal ozonides which they calculated.

The values of r_0 in Table 1 were calculated by the same investigators on the hypothesis that the unit cells of ozonides are constructed in the same way as the corresponding unit cells of azides, which was not confirmed in subsequent studies[16,26]. The author of the review also estimated the heats of formation of alkali metal ozonides from the elements by a comparative calculation[27]. Initially a check was made to find if the variation of the properties of compounds of Group I elements is linear. The following compounds were chosen for the comparison: oxides, peroxides, superoxides, hydroxides, chlorides, perchlorates, nitrates, carbonates, and sulphates. The resulting values are also listed in Table 1.

Table 1. Heats of formation of alkali metal ozonides[11].

Compound	r_0, Å	n	U, kcal	S_M*, kcal	I_M*, kcal	$-\Delta H$, kcal		
						from Ref.11	from calculated data (Ref.15)	from Ref.28
$(LiO)_3$	3.09	7	(161) (215)***	36.4	123.8	36	70±10	63±
NaO_3	3.29	8	154	26.0	118.0	45	60±10	—
KO_3	3.52	9	148	21.5	99.6	62.1**	—	—
RbO_3	3.68	10	143	20.5	95.9	62	57±10	—
CsO_3	3.84	10	137	18.8	89.4	64	57±10	—

* Data taken by Nikol'skii et al.[11] from a handbook[29].
** Value obtained from experimental data[14].
*** Estimated by Wood and D'Orazio[28].

Wood and D'Orazio[28] estimated by an extrapolation procedure the lattice energy of lithium ozonide as 215 ± 10 kcal mole^{-1} and from this value calculated the heat of formation of the ozonide as −63 ± 15 kcal mole^{-1}. They also estimated the absolute entropy and the free energy of formation of LiO_3, which are 60 e.u. [14] and 45 kcal mole^{-1} respectively.

Using the crystallographic data of Zhdanov and Zvonkova[12], Kazarnovskii and coworkers[14] calculated the lattice energy of KO_3 as 149 kcal mole^{-1}. Knowing the lattice energy and the heat of formation of KO_3, they estimated the electron affinity of the ozone molecule as 66.5 kcal mole^{-1}. This is three times greater than for the oxygen molecule (E_{O_2} = 22 kcal mole^{-1} [30]).

Wood and D'Orazio[28] estimated the electron affinity of the ozone molecule as 44 ± 10 kcal mole^{-1} and that of the oxygen molecule as 14.9 kcal mole^{-1}. These data are much lower than those quoted in other studies[14,30]. In addition, Wood and D'Orazio[28] estimated the heat of formation of the gaseous ozonide ion: $\Delta H[O_3^-\ (\text{gas})] = -11 \pm 10$ kcal mole^{-1}.

Solomon and Kacmarek[31] showed that in the visible region the spectra of solutions of alkali metal ozonides in liquid ammonia are independent of the cation and have a characteristic maximum at 450 nm.

The reactivity of ozonides has been little investigated. The principal studies dealt with the reactivity of potassium ozonide. Alkali metal ozonides react with water according to Eqn. (5), forming oxygen and the hydroxide:

$$2MO_3(\text{solid}) + H_2O(\text{liq}) \rightarrow 2MOH(\text{solid}) + \tfrac{3}{2}O_2 . \qquad (5)$$

Hence it follows that solid ozonides may serve as sources of oxygen.

III. ALKALI METAL OZONIDES

1. Lithium Ozonide

Lithium ozonide has not been obtained in a pure form but its tetrammine $Li(NH_3)_4.O_3$ is known. The tetrammine was synthesised[32] by the reaction of an ozone–oxygen mixture containing 3% of ozone with lithium hydroxide moistened with liquid ammonia ($LiOH : NH_3 = 5 : 0.2$) at −112°. The ozone-treated hydroxide was extracted with liquid ammonia. The tetrammine of lithium ozonide was salted-out from liquid ammonia solution with trifluoromethane. After the evaporation of trifluoromethane and ammonia at −126° and −78°C respectively, the solid red residue consisted of $Li(NH_3)_4.O_3$ with a considerable admixture of LiOH. The standard enthalpy of formation of the tetrammine of lithium ozonide from the elements is -135 ± 5 kcal mole^{-1}.

Several months before the publication of this study[32], the author of the review carried out experiments on the synthesis of lithium ozonide from lithium hydroxide and lithium peroxide[33]. The system was treated with ozone at −110°C, almost at the liquefaction limit of ozone, in a reactor with a screw stirrer for 3 h. The system was extracted with liquid ammonia, after the evaporation of which a thick oily dark-orange liquid remained at the bottom of the vessel. Analysis showed that the lithium : oxygen ratio was 1 : 2.56. The results of the experiments suggest that one can reliably assume that lithium hydroxide and peroxide react with ozone to form compounds of the ozonide type, as shown by the characteristic colour and the analytical lithium : oxygen ratio.

Probably the reason why lithium ozonide is not formed by a method similar to that employed for sodium and potassium ozonides and only a tetrammine is obtained, is the small radius of the lithium ion Li^+ (0.60 Å). The complex ion $Li(NH_3)_4^+$, which is larger than Li^+, can combine with the unstable O_3^- ion.

Wood and D'Orazio[28] estimated the LiO_3 lattice energy as 215 ± 10 kcal mole^{-1}. The heat of formation of LiO_3 calculated from this value is -63 ± 15 kcal mole^{-1}. Wood and D'Orazio[28] estimated the absolute entropy of LiO_3 as 20 e.u. and the entropy and free energy of formation of LiO_3 as 60 e.u. and 45 kcal mole^{-1} respectively and from these results calculated the enthalpies and free energies of the following reactions:

$$2LiO_3 \rightarrow Li_2O + {}^5/_3 O_2 \quad \begin{matrix}\Delta H = -16 \text{ kcal mole}^{-1} \\ \Delta F = -44 \text{ kcal mole}^{-1}\end{matrix}; \qquad (6)$$

$$2LiO_3 \rightarrow Li_2O_2 + 2O_2 \quad \begin{matrix}\Delta H = -26 \text{ kcal mole}^{-1} \\ \Delta F = -46 \text{ kcal mole}^{-1}\end{matrix}; \qquad (7)$$

$$LiO_3 \rightarrow LiO_2 + O_2 \quad \begin{matrix}\Delta H = +2 \text{ kcal mole}^{-1} \\ \Delta F = -19 \text{ kcal mole}^{-1}\end{matrix}. \qquad (8)$$

2. Sodium Ozonide

Sodium ozonide was first isolated by Nikol'skii et al.[11] in 1951, In a study of the reaction of dehydrated powdered sodium hydroxide (98.2%) with an ozone–oxygen mixture (8–9% O_3) at a temperature between −50° and −60°C, they observed that[11] the alkali acquired an intense yellow colour. Extraction with liquid ammonia at the same temperatures yielded a dark-red solution from which, after evaporation of liquid ammonia, a quasicrystalline dark-red product containing up to 90% of sodium ozonide, 2–3% of sodium hydroxide, and 4.6% of water was precipitated; the water was bound to the hydroxide as a hydrate.

The authors noted that sodium ozonide is extremely unstable and decomposes at room temperature with liberation of oxygen and the formation of sodium superoxide according to the equation

$$NaO_3 \rightarrow NaO_2 + {}^1/_2 O_2 . \qquad (9)$$

According to Nikol'skii et al.[11], the process reaches completion after 53 h.

Simultaneously with the work of Nikol'skii et al.[11], Whaley and Kleinberg[15] investigated the nature of the products of the reaction of ozone with alkali metal hydroxides. They confirmed[15] the data of Nikol'skii et al.[11], according to which treatment of sodium hydroxide with ozone at −60°C results in the formation of a yellow substance soluble in liquid ammonia. In addition, Whaley and Kleinberg[15] allowed ozone to react with sodium hydroxide at room temperature and showed that the resulting yellow product is insoluble in liquid ammonia and stable at room temperature. The authors believe they obtained sodium ozonide, although it was not isolated in a pure form. Its presence in the ozone-treatment product was demonstrated by an indirect method—magnetic measurements. McLachlan et al.[17] also noted that treatment of sodium hydroxide with ozone at room temperature results in the formation of a yellow substance. They suggested that the colour is due to the presence of sodium ozonide; the ozonide did not dissolve in liquid ammonia, and the ozone-treated alkali was stable for several hours on storage in closed tubes.

Griffith et al.[34], who investigated the ultraviolet spectra (200–600 n.m.) of sodium hydroxide treated with ozone at room temperature, showed that the spectra are identical with those obtained for a solution of potassium ozonide in liquid ammonia. On the basis of these data, they suggested that sodium ozonide is formed also above 0°C. In addition it was established[15,35] that, when sodium hydroxide is treated with ozone both at room temperature and below 0°C, the superoxide NaO_2 is formed together with the ozonide.

Evidently the data on the synthesis and properties of sodium ozonide are contradictory. Nikol'skii et al.[11] isolated sodium ozonide synthesised at −60°C; it is soluble in liquid ammonia and unstable at room temperature. Whaley and Kleinberg[15] and other investigators[17,34] confirmed these data and showed in addition that the reaction of ozone with sodium hydroxide takes place also at room temperature. Sodium hydroxide treated with ozone at room temperature is stable but sodium ozonide could not be extracted from it with liquid ammonia. Whaley and Kleinberg[15] put forward two explanations. The first is that sodium ozonide may exist in two crystalline forms. This hypothesis was not confirmed by experiment. The second explanation is that, in the reaction between ozone and sodium hydroxide at room temperature, the yield of sodium ozonide is extremely low and its particles are surrounded and protected by sodium hydroxide, which prevents their thermal decomposition and hinders the solubility of the ozonide in liquid ammonia, but this is unlikely.

Subsequently the possibility of the formation of sodium ozonide both above and below 0°C was demonstrated[36]. Moreover it was shown that, in the reaction with ozone, sodium superoxide is formed together with the ozonide. The study of the extraction of sodium ozonide from ozone-treated sodium hydroxide with liquid ammonia showed that the isolation of sodium ozonide synthesised above 0°C involves greater experimental difficulties than the isolation of sodium ozonide synthesised at negative tempera-

tures. The difficulties consist in the fact that sodium ozonide synthesised above 0°C instantly decomposes when the stream of ozone is stopped. The yellow colour of the product remaining after the decomposition of sodium ozonide is due to the presence of sodium superoxide formed in the reaction with ozone. Probably this is in fact the source of the above contradictions concerning the different properties of sodium ozonide synthesised at different temperatures.

The studies[36] on the preparation of sodium ozonide via sodium superoxide showed that, as with potassium and caesium[37], the reaction $MO_2 + O_2 \rightarrow MO_3 + O_2$ is possible also for NaO_2. However, the reaction of ozone with sodium superoxide is only of theoretical value for the explanation of the mechanism of the reaction with ozone owing to the low yield of the ozonide and the difficulty of carrying out the process[36].

Differential thermal analysis of sodium ozonide[38] showed that its decomposition is accompanied by an exothermic effect at $-10° \pm 2°$, due to the vigorous evolution of oxygen; this is consistent with the nature of the thermal decomposition of other alkali metal ozonides. Comparison of the heating curves for alkali metal ozonides reveals a regular increase of thermal stability with increasing atomic number of the element.

Thermogravimetric study of sodium ozonide[38] on a McBain balance made it possible to determine the degree of conversion of sodium ozonide and the rate of its decomposition at −10°, −20°, 0°, and +10°C. It is striking that the highest rate of decomposition of the ozonide is observed at the beginning of the decomposition process. Thermal decomposition of NaO_3 at −20° and −10°C proceeds up to the formation of NaO_2. Above 0°C the thermal decomposition of sodium ozonide is accompanied by the reaction of the NaO_2 formed with the water of crystallisation present in sodium ozonide and proceeds up to the formation of NaOH. At −20° and −10°C water does not enter into the reaction. The density[30] of NaO_3 is in the range 1.56−1.60 g cm^{-3}. The bright brown-red crystals of sodium ozonide exhibit pleochroism in polarised light: the crystals are coloured pale-yellow in the N_p direction and red-brown in the N_g direction. The sodium ozonide crystals are monoaxial and positive. The refractive indices are $N_p = 1.405$ and $N_g = 1.49$.

It should be noted that analysis of sodium ozonide involves considerable experimental difficulties. Direct sampling is impossible because of the extreme instability of sodium ozonide at room temperature. Therefore a special technique was developed for the analysis of sodium ozonide[40], which was subsequently employed for the analysis of other unstable ozonides.

In a preliminary X-ray diffraction study[41] a tetragonal cell with the parameters $a = 10.43$ Å, $c = 6.88$ Å, and $c/a = 0.660$ was provisionally ascribed to sodium ozonide. In a later investigation[52] these values were revised. Indexing of the X-ray diffraction patterns by means of Hall's curves yielded satisfactory agreement between the measured interplanar spacings and the values calculated for a body-centred tetragonal lattice with the ratio $c/a = 0.660$ and the parameters $a = 11.65$ Å and $c = 7.66$ Å. The space group $I4/mmm$ was chosen provisionally.

3. Potassium Ozonide

Potassium ozonide was first isolated in a crystalline state in 1949 by Kazarnovskii et al.[10] in the reaction of an ozone−oxygen mixture with potassium hydroxide below 0°C followed by extraction with liquid ammonia. The preparations obtained contained up to 83−88% KO_3 with KOH as the main impurity. In recent years a number of studies were carried out in order to find new methods for the synthesis of potassium ozonide. It was shown that potassium ozonide can be formed above 0°C at +5°C [43] and +40°C [44]. The highest yield of potassium ozonide was achieved when ozone was allowed to react with powdered potassium hydroxide in a fluidised bed[43,44]. It was shown[44] that the fluidised bed method makes it possible to extend greatly the temperature range in which potassium hydroxide can react with ozone not only in the anhydrous state, but also in the hydrated form.

The synthesis of potassium ozonide at positive temperatures is important for practical purposes. Potassium ozonide is also formed when ozone is allowed to react with potassium alkoxides[45,46]. In the reaction of ozone with potassium t-butoxide and t-perbutoxide, KO_3 is formed in yields of about 10 and 40% respectively. However, the ozonide cannot be isolated with liquid ammonia from the ozone-treated alkoxides, since the alkoxides are also soluble in ammonia[45,46]. In addition, potassium ozonide can be obtained by treating potassium superoxide with ozone[37,45,47,48]. The studies carried out in the Laboratory of Peroxy-Compounds at the Institute of General and Inorganic Chemistry of the USSR Academy of Sciences[37] and based on the estimation of the heat of the reaction

$$KO_2 + O_3 \rightarrow KO_3 + O_2 + 28 \text{ kcal} \qquad (10)$$

showed that, when KO_2 is treated with ozone at 40°C, potassium ozonide is formed in the same yield as in the reaction of ozone with potassium hydroxide and can also be successfully extracted with liquid ammonia.

Other methods for the synthesis of potassium ozonide are known[9,17,49]. Among the available methods, treatment with ozone of a suspension of potassium hydroxide[50] and particularly a suspension of KO_2 in Freons[51] is of considerable interest. The yield of potassium ozonide in the reaction of ozone with potassium hydroxide by the method of Kazarnovskii and coworkers[10] and in the reaction of ozone with potassium superoxide in a fluidised bed set up by a stream of ozonised oxygen[37] does not exceed 5−9%. The yield of the ozonide is largely promoted by two factors—an increase in the area of contact with ozone and an increase in the concentration of ozone.

A method involving the reaction of ozone with potassium superoxide in the liquid phase was developed to intensify the process. Freon-12 [52], which exhibits selective solubility in relation to an ozone-oxygen mixture, dissolving ozone alone, was employed as a solvent for ozone; in addition, it is inert with respect to KO_2 and KO_3. It has been shown[51] that, in the reaction of ozone with potassium superperoxide suspended in Freon-12, an ozonide product containing up to 80% KO_3 is obtained without extraction with liquid ammonia. Potassium ozonide was analysed by the method of Petrocelli and Capotosto[53]. The new method for the synthesis of alkali metal ozonides in Freons leads to the possibility of obtaining concentrated oxonides in a single stage without extraction with liquid ammonia and evaporation in a vacuum.

Potassium ozonide is a red crystalline substance stable only on storage in a hermetically sealed container below 0°C. The study of the kinetics of the spontaneous decomposition of potassium ozonide by chemical methods[13] showed that the reaction proceeds according to the equation $2KO_3 \rightarrow 2KO_2 + O_2$ and has the following thermodynamic parameters: $\Delta H^\circ_{298} = -11.6$ kcal, $\Delta S^\circ_{298} = 33$ e.u., and $\Delta F^\circ_{298} = -21.6$ kcal.

The dissociation of potassium ozonide is an irreversible reaction. The decomposition of KO_3 is autocatalytic with an induction period of 1.67, 20.54, and 205 days at +18.0°, −9°, and −18°C. In the subsequent active period, the rate of decomposition of potassium ozonide increases sharply; the activation energy is 22−23 kcal mole^{-1}. It has been shown by electron spin resonance (ESR) [19] that the decomposition of KO_3 at 22°C over a period between 2 and 7 days takes place approximately according to an exponential law with a time constant of 0.02 h^{-1}. It was established by differential thermal analysis [54] that the limit of the thermal stability of potassium ozonide is at 60° ± 2°C. At this temperature KO_3 is entirely converted into KO_2. To elucidate the mechanism of the decomposition of potassium ozonide, magnetic measurements were made [55] at room temperature and at 0°C. The observed deviations from additivity, which are far outside the limits of the error of the measurements, suggest the intermediate formation of a highly paramagnetic product. It is reasonable to postulate that this product is atomic oxygen, the magnetic susceptibility of which is several times greater than those of KO_3 and KO_2.

At the beginning of the decomposition the oxygen content in the solid phase increases, passes through a maximum when the degree of decomposition of potassium ozonide is about 60%, and then falls to zero for 100% decomposition. The two main elementary steps in the decomposition of potassium ozonide to potassium superoxide and oxygen may be described by the following equations:

$$\begin{gathered} KO_3 \rightarrow KO_2 + O, \\ KO_2 + O \rightarrow KO_2 + O_2, \\ \hline 2KO_3 \rightarrow 2KO_2 + O_2. \end{gathered}$$

The density of potassium ozonide is 1.990 g cm^{-3} [39]. Externally potassium ozonide crystals do not exhibit cleavage planes, the grains are formless, and show pleochroism, noted in an earlier study by Azarov and Korvin [16]. They are coloured pale-yellow in the N_p direction and red-brown in the N_g direction. The crystals are monoaxial, negative, and exhibit appreciable double refraction. The refractive indices are $N_p = 1.391$ and $N_g = 1.670$. The heat of formation of KO_3 was determined by measuring its heat of solution in dilute sulphuric acid [14] and amounts to 62.1 ± 0.9 kcal mole^{-1}.

The solubility of potassium ozonide in liquid ammonia was measured in two ways. In a study of the phase diagram for the NH_3-KO_3 system by an isothermal method, and by visual observations over a range of temperatures [56] (the "visual polythermal" method), it was established that the maximum solubility of 14.82 g/100 g NH_3 is attained at −35°C. Determinations of the vapour pressures of saturated solutions of potassium ozonide in liquid ammonia established [32] that the solubility of KO_3 at −63.5°C is approximately 12 g/100g NH_3.

Potassium ozonide is a powerful oxidant and contains 46 wt.% of active oxygen. It reacts instantly with water both at room temperature and at 0°C, with liberation of oxygen via the intermediate formation of OH radicals. In a study of isotope exchange between free hydroxy-radicals and water in 1957, Kazamovskii et al. [57] proposed the following mechanism for reaction (5):

$$\begin{gathered} KO_3 + H_2O^x = KO^xH + O_2, \\ \cdot OH + H_2O^x = \cdot{}^xOH + H_2O, \\ \cdot O^x H + \cdot O^x H = H_2O^x + {}^3/_2\, O_2^x, \\ \cdot O^x H + \cdot OH = H_2O_2^x. \end{gathered} \qquad (11)$$

Not more than 15% of the hydroxy-radicals are converted into H_2O_2 by reaction (11).

The reaction of hydroxy-radicals generated by potassium ozonide with hydrogen peroxide solution was investigated at 0°C [58]. When KO_3 is introduced into water, instantaneous reaction with liberation of oxygen and the formation of KOH and H_2O_2 is observed. The degree of consumption of OH in the formation of H_2O_2 is 18−24%. In hydrogen peroxide solutions, the formation of H_2O_2 is less pronounced and at $[H_2O_2] = 0.3$ M becomes zero.

A mixture of potassium ozonide powder and ice was investigated by the ESR method with slow increase of temperature from −196° to 0°C [59]. As the mixture is gradually heated to a temperature slightly above 0°C, a sharp decrease of signal intensity and the appearance against its background of a narrow signal with a g- factor of 2.011 are observed. The authors [59] believe that the observed signal is probably due to free hydroxy-radicals formed in the reaction of potassium ozonide with water:

$$KO_3 + H_2O \rightarrow KOH + OH + O_2. \qquad (12)$$

The reactions of formic and acetic acids with hydroxy-radicals and molecular oxygen, generated by potassium ozonide, have been investigated. The experiments at room temperature with aqueous formic acid solutions yielded carbon dioxide, oxygen, and hydrogen peroxide as the products. The reaction with anhydrous formic acid results in the formation of carbon dioxide, oxygen, carbon monoxide, and hydrogen [60]. The reaction with acetic acid vapour is instantaneous, goes virtually to completion, and is accompanied by a blue luminescence. The principal products are carbon dioxide, carbon monoxide, molecular hydrogen, water, and a small amount of methane [61]. Potassium ozonide is inert with respect to F_2O_3 dissolved in Freon-13 in the temperature range between −183° and 103° [62]. The reaction of potassium ozonide with water vapour and carbon dioxide was studied in greater detail. In the temperature range 0−20°C, potassium ozonide reacts vigorously with water vapour, active oxygen being completely liberated with formation of potassium hydroxide dihydrate [63]. At +24°C and 50% humidity potassium ozonide grains fully decompose in 30 h under the action of water vapour. During the first two hours, 87% of oxygen is removed. The average rate of liberation of oxygen during the active period is 10.9 ml g^{-1} h^{-1} but at the same temperature and 100% humidity the average rates of evolution of oxygen is 29.6 ml g^{-1} h^{-1}. [64]

The reaction of potassium ozonide with carbon dioxide takes place only in the presence of water vapour via a stage involving the complete hydrolysis of the ozonide with subsequent formation of potassium carbonate and its hydrates. The rate of evolution of oxygen is determined by the rate of diffusion of water vapour [63,94]:

$$\begin{gathered} 2KO_3 + H_2O \rightarrow 2KOH + {}^5/_2\, O_2, \\ 2KOH + CO_2 \rightarrow K_2CO_3 + H_2O. \end{gathered} \qquad (12a)$$

In the absence of moisture the reaction between KO_3 and CO_2 does not occur. The potassium bicarbonate present in the reaction products is determined by potentiometric titration with acid. The ready formation of potassium carbonate increases the possible usefulness of potassium ozonide as a life-supporting agent [64].

Zhdanov and Zvonkova [12] found from the X-ray diffraction pattern of the powder that potassium ozonide has a lattice close to the tetragonal lattice of potassium azide (KN_3) with the parameters $a = 6.094$ Å and $c = 7.056$ Å. However, the absence from the diffraction pattern of the important reflection with an index of 121, according to their data, does not confirm the hypothesis of a linear configuration of the O_3^- ion. Therefore they believe [12]

that the symmetry of KO_3 is probably lower than that of KN_3. In the light of new data on the structure of the ozone molecule [23], it has been suggested that the KO_3 lattice may be of a different type. As stated above, Smith [23] found that the O_3^- ion is not linear but angular with an angle of 110° ± 5° and $r = 1.34 \pm 0.05$ Å. Since these values are close to the corresponding data for the NO_2^- ion, for which the angle $<O-N-O = 115° \pm 4°$ and $r = 1.34 \pm 0.03$ Å, Smith postulated that the structures of KO_3 and KNO_2 are similar. On the basis of the correspondence of the X-ray diffraction data (l and d) for KO_3 and KNO_2, he believes it to be likely that KO_3 has a monoclinic unit cell of the KNO_2 type and with the same coordination.

Azarov and Korvin [16] showed that potassium ozonide has a body-centred tetragonal unit cell with the parameters $a = 8.597 \pm 0.002$ Å and $c = 7.08 \pm 0.002$ Å; the space group is $I4/mcm$. In view of the similarity of the reflection intensities of KO_3 and KN_3, they believe that these structures are derived from the CsCl structure, where each N_3^- or O_3^- ion occupies a Cl^- site and K^+ occupies a Cs^+ site. They calculated from the coordinates of the atoms that the O_3^- ion is not linear but angular with an angle of 100° and $r = 1.19$ Å.

4. Rubidium Ozonide

Rubidium ozonide was first isolated in 1951 by Nikol'skii et al. [11] The reaction between rubidium hydroxide and ozone was carried out at −30°C with subsequent extraction by liquid ammonia. After the evaporation of liquid ammonia, orange quasi-crystalline rubidium ozonide preparations were isolated with an RbO_3 content between 55 and 66% (the residue was RbOH).

The high percentage of the impurity is due to the considerable solubility of RbOH in liquid ammonia (at −40°C 100 ml of liquid ammonia dissolves 0.9 g of RbOH).

In 1966 96.6% pure rubidium ozonide was obtained [65]. This high rubidium ozonide content was achieved by employing as the starting material rubidium superoxide (93.3%), which in turn was prepared by atomising metallic rubidium in an oxygen and argon atmosphere with the aid of a special sprayer and apparatus described in detail by Vol'nov and Matveev [66]. The reaction of ozone with rubidium superoxide was carried out at 0°C for 50 min in a fluidised bed set up with a stream of ozonised oxygen. Before extraction the ozone-treated rubidium superperoxide contained 70.5% RbO_3.

At room temperature rubidium ozonide decomposes slowly according to the equation

$$RbO_3 \rightarrow RbO_2 + {}^1/_2 O_2 . \qquad (13)$$

The density of rubidium ozonide is 2.75 g cm^{-3} [67]. Polycrystalline RbO_3 specimens exhibit pleochroism; they are coloured pale-yellow in the direction of the smallest refractive index and dark-brown in the direction of the largest refractive index; $N_p = 1.456$, $N_m = 1.576$, and $N_g = 1.750$. The rubidium ozonide crystals are optically biaxial.

The solubility of rubidium ozonide in liquid ammonia in the temperature range between −48° and −84° has been investigated. The RbO_3-NH_3 system is of the type with a simple eutectic at a temperature between −82° and −83°C. The eutectic mixture contains 4.0% RbO_3 (4.3 g of RbO_3 in 100 g of NH_3). [68]

5. Caesium Ozonide

The literature data on the synthesis of caesium ozonide up to 1963 may be regarded as merely exploratory, since pure caesium ozonide had not been obtained up to that time.

In a study of the reaction of ozonised oxygen with CsOH, Manchot and Kampschulte [8] noted that CsOH becomes coloured red, the colour disappearing on subsequent heating to 140−160°C. Traube [6] carried out the reaction of ozone with carefully dehydrated CsOH at temperatures between 20° and 0°C. The coloured product was decomposed by water with evolution of 2% of oxygen and the formation of a very small amount of hydrogen peroxide. When [ozone-treated] caesium hydroxide was stored in the cold, the colour persisted for 14 days. An unstable coloured product with the empirical composition CsOH.O was obtained by Strecker and Thienemann [69] in the reaction of ozone with a solution of metallic caesium in liquid ammonia. Because of the considerable solubility of CsOH in liquid ammonia (1.0 g/100 ml NH_3), the purest preparation obtained by Nikol'skii et al. [11] contained 67.3% $CsOH_3$ and 31.2% CsOH.

In order to prepare pure caesium ozonide, the reaction of caesium superoxide with an ozone−oxygen mixture in a fluidised bed was employed above 0°C [37,48] using the method of Vol'nov and Matveev [66]. Caesium superoxide reacted with ozone in a fluidised bed produced by a stream of an ozone−oxygen mixture containing up to 8% of ozone. After extraction with liquid ammonia, a product containing up to 92.5% of caesium ozonide was obtained [66]. Caesium ozonide is extremely unstable with respect to moisture and carbon dioxide. The caesium ozonide content in the ozone−treated superoxide and in the ozonide itself after extraction with liquid ammonia was found by determining the active oxygen and Cs_2O [48].

In order to determine the limit of the thermal stability of caesium ozonide and to discover the processes occurring during its decomposition, a differential heating curve was recorded on a Kurnakov differential thermal analyser [70]. At the same time measurements were made of the amount of oxygen evolved on heating. The heating curve showed two effects. An exothermic effect, which begins at 70°C and has a maximum at 100°C, corresponds to the decomposition of CsO_3 to CsO_2 and is accompanied by the evolution of oxygen. An endothermic effect at 408°C corresponds to the fusion of CsO_2 with subsequent decomposition to the oxide and liberation of oxygen. The density and the refractive index of caesium ozonide were measured [71]. In transmitted polarised light CsO_3 crystals are coloured dark cherry red and exhibit pleochroism. In the direction of the minimum refractive index, their colour is pale yellow, and in the direction of the maximum refractive index dark cherry red. In thick layers the crystals absorb light almost completely and become opaque. The crystals belong to the middle category and are optically monoaxial and positive. The refractive indices are $N_m = 1.523$ and $N_g = 1.69$. The density measured by hydrostatic weighing is 3.19 g cm^{-3} and the X-ray density is 3.22 g cm^{-3}. Like sodium and potassium ozonides, caesium ozonide has the lowest density compared with the peroxide and the superoxide:

	Cs_2O_2	CsO_2	CsO_3
d_4^{20}	4.47	3.80	3.19

But in the series of ozonides its density is a maximum:

	NaO_3	KO_3	RbO_3	CsO_3
d_4^{20}	1.6	1.99	2.75	3.19

Caesium ozonide crystallises with a body-centred tetragonal lattice, having the parameters $a = 9.75$ Å, $c = 8.75$ Å, and $c/a = 0.9$.[26] The space group is $I4/mcm$.

IV. ALKALINE EARTH METAL OZONIDES

The problem of the formation of alkaline earth metal ozonides remained open until recently. Manchot and Kampschulte[8] noted that, in the reaction of an ozone-oxygen mixture containing 8 wt.% of ozone with magnesium, strontium, and barium oxides at room temperature, ozone was decomposed and at −80°C barium oxide acquired an intense yellow colour, calcium oxide was less strongly coloured, and the colour of magnesium oxide was insignificant. They suggested that these coloured compounds are ozonides. However, this hypothesis was not confirmed either by chemical analysis or other methods. Blumental[72] repeated the experiments of Maschot and Kampschulte and reported the formation of "some kind" of substance which does not decolourise potassium permanganate solution but liberates iodine from acid potassium iodide solutions. Strecker and Thienemann[73] oxidised solutions of metallic barium and calcium in liquid ammonia with an ozone−oxygen mixture. With calcium, they obtained a brown precipitate, which fully decomposed on evaporation of ammonia and was not analysed. These data exhaust the early information about the products of the reaction of alkaline earth metals with ozone.

The first calcium, strontium, and barium ozonides were synthesised in 1966.[74] On the hypothesis that the reaction of ozone with alkaline earth metal hydroxides is described by the equation

$$M(OH)_2 + 2O_3 \rightarrow M(O_3)_2 + H_2O + {}^1/_2O_2 \ , \qquad (14)$$

the thermodynamic functions for this reaction with calcium, strontium, and barium hydroxides were estimated[74]. The results are presented in Table 2.

Table 2. Estimation of the enthalpies of formation of alkaline earth metal ozonides from the elements and the enthalpy and free energy of reaction (14) (±10 kcal).

Compound	ΔH^0_{298} for formation from elements	By reaction (14)	
		ΔH^0_{298}	ΔF^0_{298}
$Ca(O_3)_2$	−169	−69	−83
$Sr(O_3)_2$	−161	−68	−81
$Ba(O_3)_2$	−157	−67	−80

The values of ΔH°_{298} for the formation of the ozonides from the elements were estimated by comparative calculation[27]. It was shown[74] that, in the reaction of ozone with calcium, strontium, and barium hydroxides at −100°C, the latter become coloured yellow, the colour intensity increasing from calcium to barium.

An ESR study of the resulting coloured precipitates at the temperature of liquid nitrogen showed the presence of a typical spectrum of the ozonide ion with $g = 2.01$. The thermal stability of the ozonides increases from calcium to barium. Calcium ozonide decomposes appreciably at −35°C, strontium ozonide a little below 0°C, and barium ozonide at 0°C.

The results of the ESR study suggest that the coloured products are formed in the reaction of the ozone−oxygen mixture with solid alkaline earth metal hydroxides and are ozonides containing the paramagnetic ion O_3^-.

V. AMMONIUM AND TETRAMETHYLAMMONIUM OZONIDES

The capacity for the formation of an ozonide is not characteristic solely of alkali and alkaline earth metals but also of the ammonium ion and its derivatives.

In 1907 Manchot and Kampschulte[8] were the first to predict the possibility of the existence of ammonium ozonide. They found that, when dilute ozone is passed through liquid ammonia, a dark-orange colour is produced, which persists until the liquid is heated. They discovered that the colour is most intense at −70°C and disappears at −60°C. Strecker and Thienemann[7] also observed a short-lived colour when dilute ozone was passed through liquid ammonia, although the product isolated contained mainly ammonium nitrate. Experiments carried out in the Laboratory for Peroxy-Compounds at the Institute of General and Inorganic Chemistry on the reaction of ozone with solutions of metallic calcium in liquid ammonia showed that the solutions assume a bright-orange colour which gradually disappears as ammonia is evaporated[75].

Ammonium ozonide was first isolated in 1962 by Solomon et al.[76] by the reaction of ozone with liquid ammonia at a temperature below −100°C. The absorption spectrum of ammonium ozonide in a mixture with trifluoromethane is analogous to the spectra of other ozonides. The use of a solvent was necessary to keep the system in the liquid state at the low temperature required for the stabilisation of ammonium ozonide. A peak at 450 nm, characteristic of the ozonide ion, was observed in the spectrum of ammonium ozonide. Moreover, the ESR spectra of potassium, tetramethylammonium, and ammonium ozonides were recorded to identify ammonium ozonide. The presence of the ozonide ion was demonstrated in all these compounds. The results are presented in Table 3.

Table 3.

Compound	g-factor
KO_3	2.0124
$(CH_3)_4NO_3$	2.0144
NH_4O_3	2.0119

Ammonium ozonide is stable only below −126°C. It decomposes according to the equation

$$2NH_4O_3 \rightarrow NH_4NO_3 + {}^1/_2O_2 + 2H_2O \ . \qquad (15)$$

Herman and Giguere[18] also showed that ammonium ozonide begins to decompose at temperatures below −126°C and at −90°C the decomposition is complete.

In 1929 Traube and Kyhbier[77] treated tetramethylammonium hydroxide with ozone and obtained a red substance to which they attributed the formula $(CH_3NOH)_2.O_2$. Tetramethylammonium ozonide was first isolated and identified by Solomon et al.[78] It was obtained by the reaction of ozone with tetramethylammonium hydroxide at

25°C. The absorption spectrum of the solution of tetramethylammonium ozonide in liquid ammonia has an absorption maximum at 450 nm, characteristic of all ozonides.

Tetramethylammonium ozonide dissolves in liquid ammonia at −63°C to the extent of 1.3 ± 1 g/100 g NH_3. It is stable up to 25°C and at 25°C decomposes completely over a period of 48 h. The heat of formation of $[N(CH_3)_4]O_3$ from the elements is 49.5 ± 4 kcal mole^{-1}.

VI. SOME HYPOTHESES CONCERNING THE MECHANISM OF THE FORMATION OF OZONIDES

The formation of alkali metal ozonides by the mechanism proposed by Kazarnovskii[11,79] proceeds via an unstable complex of the type $M^+O^-H^+O_3^-$ and a subsequent further reaction with ozone:

$$2\,MOH + 2\,O_3 \rightarrow 2\,MOH \cdot O_3\,, \quad (16)$$
$$2\,MOH \cdot O_3 + 2\,O_3 \rightarrow 2\,MO_3 + 2\,HO_2 + 2\,O_2\,, \quad (17)$$
$$2\,HO_2 \rightarrow H_2O + 1.5\,O_2\,, \quad (18)$$
$$MOH + H_2O \rightarrow MOH \cdot H_2O\,, \quad (19)$$
$$3\,MOH + 4\,O_3 \rightarrow 2\,MO_3 + MOH \cdot H_2O + 3.5\,O_2\,. \quad (20)$$

The overall result is the formation of a mixture of the alkali metal ozonide and the monohydrate of the hydroxide with a simultaneous conversion of a large amount of ozone into oxygen. The activation energy for the reaction of potassium hydroxide with ozone has been estimated as 3.1 kcal.[80]

The following considerations can be put forward concerning the above mechanism for the formation of alkali metal ozonides. The mechanism is based on two hypotheses: the hypothesis of the formation of the unstable complex $MOH.O_3$ of sodium, potassium, rubidium, or caesium (but not lithium) hydroxides with an ozone molecule [reaction (16)] and the hypothesis of the participation of the radical HO_2 [by reaction (17)] in the formation of the ozonides of these elements.

According to Eqn. (20), the ratio of the metal hydroxide monohydrate to the ozonide is 1:2, which means that in the reactions of ozone with sodium and potassium hydroxides the ozonide contents should be 71% and 66.4% respectively. However, it has been shown that not more than 4−5% NaO_3 is detected in the ozone-treated sodium hydroxide[36,81]. This contradiction was eliminated in a mechanism for the formation of ozonides put forward subsequently[82]. Probably the reaction of ozone with alkali metal hydroxides takes place mainly on the surfaces of the solid hydroxides. Isotopic analysis of oxygen in potassium ozonide[75] synthesised from $K^{18}OH$ with the natural composition showed that the oxygen of the hydroxide is involved in the formation of the ozonide.

On the basis of the fact that potassium ozonide is formed also by the reaction $KO_2 + O_3 \rightarrow KO_3 + O_2$ from the superoxide and ozone[11,37,83] and data[80] for the catalytic decomposition of ozone on the KOH surface, it is more probable that atomic oxygen is responsible for the formation of ozonides.

The mechanism proposed for the formation of ozonides[82] presupposes the successive occurrence of the following reactions:

$$3\,O_3 + 2\,MOH \rightarrow 3\,O_2 + 2\,MOH \cdot O + O\,, \quad (21)$$
$$2\,MOH \cdot O + O \rightarrow 2\,MO_2 + H_2O\,, \quad (22)$$
$$2\,O_3 + 2\,MO_2 \rightarrow 2\,MO_2 \cdot O + 2\,O_2\,, \quad (23)$$
$$2\,MO_2 \cdot O \rightarrow 2\,MO_3\,, \quad (24)$$
$$5\,O_3 + 2\,MOH \rightarrow 5\,O_2 + 2\,MO_3 + H_2O\,. \quad (25)$$

Reaction (21) has been confirmed by the data of Schwab and Hartman[80] and the results obtained in a study of the reaction of ozone with sodium hydroxide[36]. The occurrence of reaction (22) has been demonstrated in a study of the reaction of potassium hydroxide with atomic oxygen generated in a glow discharge[84]. Reactions (23) and (24) are components of reaction (10). The overall equation (25) is based on the three experimentally demonstrated intermediate reactions and is consistent with the decomposition of ozone in which n moles of oxygen and n atoms of oxygen should be formed from n moles of ozone.

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The data presented in the review show that recently there has been a considerable growth of interest in compounds included in the class of inorganic ozonides. The chemistry of ozonides has been attracting the attention of investigators both in the Soviet Union and abroad.

Evidently the main studies are devoted to problems of the synthesis, structure, and physicochemical properties of ozonides. Very few investigations deal with the reactions of these substances with various classes of compounds: solid, liquid, gaseous, inorganic, and organic. There has been no work at all on the stabilisation of ozonides.

The study of these processes will characterise more fully this new class of compounds and will bring nearer their practical application. The accumulation of experimental data on the synthesis and properties of ozonides and the mechanisms of their formation will help in the elucidation of the mechanism of the formation of important inorganic radicals.

Inorganic ozonides, which are powerful oxidants and sources of oxygen, are very promising substances and further intensification of the study of their synthesis and properties and also ways for their stabilisation will lead to their wider practical application.

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Electron Spin Resonance Spectra of Fluorocarbon Radicals

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A systematic account has been given of the information currently available about the components of the hyperfine coupling tensor of fluorocarbon radicals and also information about the form of the spectra of fluorocarbon radicals containing one and two α-fluorine atoms in polycrystalline specimens. Recent information on the paramagnetic centres in irradiated polytetrafluoroethylene, including fluorocarbon radicals and also radicals formed in their oxidation, is presented. The bibliography includes 24 references.

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I. INTRODUCTION

Fluorocarbon compounds are finding increasing application in a wide variety of branches of the national economy. In this connection it is particularly necessary to obtain information about the processes occurring which involve fluorocarbon radicals.

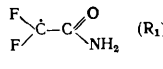
The studies on fluorocarbon radicals by the ESR method have specific features and present certain difficulties. So far the number of unambiguously identified fluorocarbon radicals does not exceed several tens and even as regards the identification of the most thoroughly studied magnetic centres (PC) there exist various mutually exclusive views.

In the present review an attempt is made to give a systematic account of certain radiospectroscopic data on a number of fluorocarbon paramagnetic centres. The first part of the review deals with the available data on the components of the hyperfine coupling tensor of fluorocarbon radicals obtained in the study of irradiated single crystals. The characteristics of the spectra of radicals with one or two α-fluorine atoms in polycrystalline specimens are discussed. The second part of the review considers the results from studies of paramagnetic centres in irradiated polytetrafluoroethylene (PTFE).

II. HYPERFINE COUPLING CONSTANTS OF FLUOROCARBON RADICALS

The broadening of the ESR spectra of fluorocarbon radicals in polycrystalline specimens is caused mainly by hyperfine anisotropic coupling. In order to understand the characteristic features of such spectra, it is extremely important to have information about the constants of the hyperfine coupling tensor for α- and β-fluorine atoms. The values of the constants for α-fluorine atoms in some radicals are presented in the Table

Analysis of the spectra of an irradiated single crystal led Lontz and Gordy[1] to the conclusion that in the radicals



(R₁)

the fragment $\diagdown C-\dot{C}F_2$ is planar and is probably located in the plane of the CON group.

If the magnetic field H_0 is perpendicular to the plane of the crystal, the ESR spectrum consists of three lines with a splitting of 178 Oe between the components. If the field H_0 is in the plane of the radical, a triplet is also observed but the splitting between the components is 24 Oe. In this triplet the splitting is independent of the angle between the direction of the C–C bond in the radical and the direction of the external field.

Constants of the hyperfine coupling tensors

Radical	Constants of HFC tensor for α-F atoms, Oe				Radical	Constants of HFC tensor for α-F atoms, Oe			
	A_1	A_2	A_3	$\bar{A}$		A_1	A_2	A_3	$\bar{A}$
$\dot{C}F_2CONH_2$	178	24	24	75	$CF_3\dot{C}FCONH_2$	201	12	8	74
$\dot{C}HFCONH_2$	189	−4	−16	56	$CO_2^-CF_2\dot{C}FCO_2^-$	150	59	4	71

In the R_1 radical the unpaired electron density is mainly localised at the C–C molecular orbital. At first sight it might appear that, for certain orientations of the magnetic field, the fluorine atoms should be non-equivalent and consequently the spectrum should consist of four lines. However, it is found that, for any orientation, the spectrum consists of three lines the splitting between which depends on the orientation of the radical. The authors believe that the hyperfine coupling constants are due mainly to the unpaired electron density at the fluorine nucleus.

The ESR spectrum of the R_1 radical can be described by the Hamiltonian

$$\mathbf{H} = \beta\,\mathbf{S}\mathbf{g}\mathbf{H}_0 + \sum_{i=1}^{2} \mathbf{S}\mathbf{A}_i\,\mathbf{I}_i - \sum_{i=2}^{2} g_I\beta_I\,\mathbf{I}_i\mathbf{H}_0\,. \qquad (1)$$

The first term of the Hamiltonian represents the coupling between the magnetic moment of the electron and the external field, the second the coupling of the nuclear moments of the fluorine atoms with the magnetic moment of the electron, and the last term is due to the coupling between the nuclear moments of fluorine and the external magnetic field. The tensors g and A characterise the

spin–orbit and hyperfine coupling in the radical. Experiments showed that in the case under discussion the tensors g and A have axial symmetry and their axes of symmetry coincide.

The authors calculated theoretically the energy levels and the ESR spectrum for the paramagnetic centres described by the Hamiltonian (1) in the case where the electron–nucleus interaction is small compared with the interaction with the external magnetic field. The diagram of the resulting energy levels is presented in Fig. 1. The frequencies ν_1, ν_2, and ν_3 correspond to allowed transitions and ν_4, ν_5, ν_6, and ν_7 to forbidden transitions in which the orientations of the electronic and nuclear spins change.

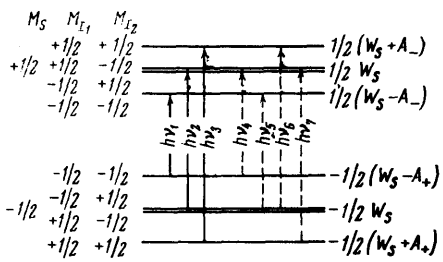


Figure 1. Diagram of energy levels due to the interaction of the unpaired electron with two equivalent fluorine nuclei in the radical $\dot{C}F_2CONH_2$. The continuous and dashed lines indicate the allowed and forbidden transitions respectively.

The splitting between the energy levels of the allowed transitions is given by the expressions

$$h\nu_1 = W_s - \frac{1}{2}(A_+ + A_-)\,,$$
$$h\nu_2 = W_s\,, \qquad (2)$$
$$h\nu_3 = W_s + \frac{1}{2}(A_+ + A_-)\,,$$

where

$$A_+ = [(A_\parallel + W_I)^2\cos^2\theta + (A_\perp + W_I)^2\sin^2\theta]^{1/2},$$
$$A_- = [(A_\parallel - W_I)^2\cos^2\theta + (A_\perp - W_I)^2\sin^2\theta]^{1/2},$$
$$W_s = g_s\beta_s H_0;\quad W_I = 2g_I\beta_I H_0\,.$$

In the case considered the hyperfine coupling tensors for both fluorine nuclei have axial symmetry and, moreover, their principal values coincide. The constant $A_\parallel = A_\perp$ corresponds to the direction of the principal axis of the tensor, which is perpendicular to the plane of the radical; θ is the angle between the direction of the external magnetic field H_0 and the normal to the plane of the radical. The splitting in the ESR spectrum between adjacent components of the triplet is given by the expression

$$t = \frac{1}{2}(A_+ + A_-)\,. \qquad (3)$$

When the magnetic field is perpendicular to the plane of the radical ($\theta = 0$), then $t = A_\parallel$. For $\theta = 90°$, $t = A_\perp = A_2 = A_3$. In the case considered the g-factor is determined by the relation familiar for the case with axial symmetry:

$$g(\theta) = (g_\parallel^2\cos^2\theta + g_\perp^2\sin^2\theta)^{1/2}\,, \qquad (4)$$

where $g_\parallel$ and $g_\perp$ correspond to the parallel and perpendicular orientations of the permanent magnetic field relative to the plane of the radical.

For the R_1 radical, the parameters of the g-tensor are

$$g_\parallel = 2.0025 \pm 0.0010\,,$$
$$g_\perp = 2.0045 \pm 0.0010\,.$$

We may note that in the 3 cm band, for the splitting of the adjacent components of the triplet, W_I may be neglected to a first approximation, particularly for directions of H_0 close to those of the principal axes of the tensor, and Eqn. (3) becomes

$$t = A = [A_\parallel^2\cos^2\theta + A_\perp^2\sin^2\theta]^{1/2}.$$

The average value of the principal components of the hyperfine coupling tensor corresponding to isotropic hyperfine coupling is

$$\bar{A} = \pm\frac{1}{3}(A_\parallel + 2A_\perp)\,.$$

For splittings between adjacent components, one can obtain approximately

$$A = \bar{A} + A_\mu(3\cos^2\theta - 1)\,,$$

where

$$A_\mu = \pm\frac{1}{3}(A_\parallel - A_\perp)\,.$$

The frequencies of the forbidden transitions, indicated in Fig. 1 by dashed lines, are given by the expressions

$$h\nu_4 = W_s - \frac{1}{2}A_+\,,$$
$$h\nu_5 = W_s - \frac{1}{2}A_-\,,$$
$$h\nu_6 = W_s + \frac{1}{2}A_-\,, \qquad (5)$$
$$h\nu_7 = W_s + \frac{1}{2}A_+\,.$$

The ratio of the probability of forbidden transitions to the probability of allowed transitions is

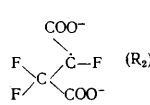
$$r = \frac{C^2(A_+ - A_- + 2W_I)^2}{(A_{ZZ} + A_- - W_I)(A_{ZZ} + A_+ + W_I) + C^2}\,, \qquad (6)$$

where

$$A_{ZZ} = A_\parallel\cos^2\theta + A_\perp\sin^2\theta\,,$$
$$C^2 = (A_\parallel - A_\perp)^2\sin^2\theta\cos^2\theta\,.$$

It is easily seen from Eqn. (6) that the probability of the forbidden transitions depends significantly on the difference $A_\parallel - A_\perp$ and on the value of W_I. For fluorocarbon radicals, the anisotropy characterised by the value of $A_\parallel - A_\perp$ is very high and the forbidden transitions make a significant contribution to the observed spectrum,

In the 8 mm band for certain orientations of the radical, the intensity of the spectra due to the forbidden transitions is comparable to that of the spectra corresponding to the allowed transitions. As an example, Fig. 2 presents the ESR spectra of the radicals



(R_2)

obtained in an irradiated single crystal[2]. For the chosen orientation of the single crystal, two groups of lines consisting of four components are seen on the second derivative absorption spectrum obtained in the 3 cm band (Fig. 2*a*). The splitting between the centres of these groups is due to the interaction with the one α-fluorine atom and the splitting into four components within the

groups is due to interactions with the two non-equivalent β-fluorine atoms.

In the spectrum obtained for the same orientation using the 8 mm band, the components corresponding to the forbidden transitions are very intense (Fig. 2*b*).

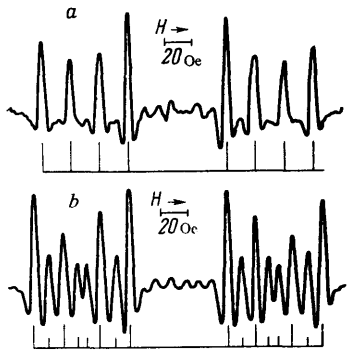
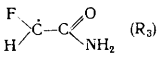


Figure 2. Second derivative absorption spectra for a certain orientation of the radical $CO_2-CF_2\dot{C}FCO_2-$ in a magnetic field H_0 in the 3 cm (curve *a*) and 8 mm (curve *b*) wavelength ranges.

It proved possible to obtain information about the components of the hyperfine coupling tensors for both α- and β-fluorine atoms of the radicals R_2. The anisotropy for the β-fluorine atom is significantly lower than for the α-atoms. The principal values of the hyperfine coupling tensor components for one of the β-fluorine atoms are 63, 23, and 19 Oe and those for the other β-fluorine atom are 71, 27, and 23 Oe.

It is noteworthy that, for reasons which are insufficiently clear, in R_2 the symmetry of the hyperfine coupling tensor for the α-fluorine atom differs from the axial symmetry.

The hyperfine coupling constants of the radicals

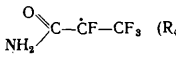


(R3)

in irradiated single crystals have been investigated. It was found that the symmetry of the hyperfine coupling tensor for the fluorine atom differs somewhat from axial symmetry. By analysing the spectra in the 3 cm and 8 mm bands, the authors succeeded in demonstrating that the isotropic hyperfine coupling constant is positive and equal to 56 Oe. The principal values of the hyperfine coupling tensor for the fluorine atom proved to be 189, −4, and −16 Oe. The highest value of the component corresponds to the principal axis of the tensor being oriented perpendicular to the plane of the radical. The tensor component equal to −16 Oe corresponds to the direction of the principal axis along the C–F bond of the radical.

The authors estimated the contribution to the tensor components due to the unpaired electron density in the $2p_\pi$ carbon orbitals, the $2p_\delta$ fluorine orbital (the orbital responsible for the C–F δ-bond), and the $2p_\pi$ orbital of the fluorine atom. It was found that, although the unpaired electron density in the $2p_\pi$ carbon orbital is very high, the contribution of this orbital to the largest tensor component is insignificant.

Fluorocarbon radicals containing β-fluorine atoms have also been investigated[4]:



(R4) .

It was found that in the R_4 radical the CF_3 group is rotating at room temperature and each β-fluorine atom has the same values of the principal components of the hyperfine coupling tensor, equal to 36, 17, and 14 Oe. The principal values of the hyperfine coupling tensor components for the α-fluorine atom are 201, 12, and 8 Oe.

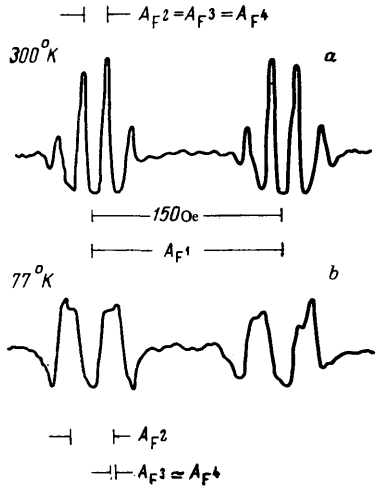


Figure 3. Second derivative absorption spectra for a certain orientation of the radical $CF_3\dot{C}FCONH_2$ in a magnetic field H_0: *a*) 300°K; *b*) 77°K.

Fig. 3 presents the spectra at 300° and 77°K corresponding to a certain orientation of the R_4 radical.

We may note that a decrease of temperature has hardly any effect on the splitting due to the α-fluorine atom. However, the structure due to the interaction with β-fluorine atoms changes significantly.

It follows from the analysis of the spectrum in Fig. 3*b* that at 77°K the rotation of CF_3 is frozen and one of the β-fluorine atoms has higher hyperfine coupling constants than the other two, which may be regarded as equivalent.

III. ESR SPECTRA OF FLUOROCARBON RADICALS IN POLYCRYSTALLINE SPECIMENS

The data for the hyperfine coupling constants of fluorocarbon radicals discussed in the preceding section make it possible to account for the specific features and the form of their ESR spectra in polycrystalline specimens.

The hyperfine coupling constants of fluorocarbon radicals due to α-fluorine atoms are significantly higher than the constants due to β-fluorine atoms. The anisotropic hyperfine interactions of α-fluorine atoms are very large compared with the isotropic interactions. In this connection the broadening of the ESR spectra of fluorocarbon radicals in polycrystalline specimens is due mainly to anisotropic hyperfine interactions.

For hydrocarbon radicals, the overall contour of the spectrum is determined by the broadening of the isotropic hyperfine structure caused both by the anisotropy of the hyperfine coupling and the anisotropy of the g-factor.

The anisotropy of the g-factor for fluorocarbon radicals makes a significantly lower contribution to the overall contour of the spectra in polycrystalline specimens compared with the anisotropy of the hyperfine coupling.

The anisotropy of the hyperfine coupling of β-fluorine atoms is relatively low and therefore hyperfine coupling to them gives rise in the spectra to partially resolved components.

The overall spread of the spectra of fluorocarbon radicals with one α-fluorine atom is approximately equal to the maximum component of the hyperfine coupling tensor for α-fluorine atoms, which usually amounts to about 190 Oe. With two α-fluorine atoms, the spectra extend over about 400 Oe.

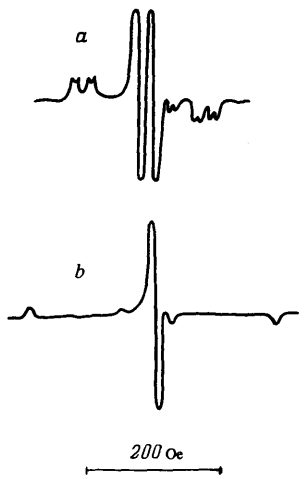
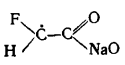


Figure 4. First derivative absorption spectra of the radicals $\dot{C}FHCOONa$ (curve *a*) and $\dot{C}F_2COONa$ (curve *b*).

The form of the spectra of fluorocarbon radicals in polycrystalline specimens in the 3 cm band may be calculated without taking into account the forbidden transitions. In the 8 mm band forbidden transitions make an appreciable contribution to the spectrum.

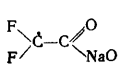
The derivative absorption spectra of radicals containing one or two α-fluorine atoms in polycrystalline specimens are presented in Fig. 4.

For the radicals



(R_5),

the spectrum shows wing components separated from one another by approximately 180 Oe (Fig. 4*a*). For the radicals



(R_6),

containing two α-fluorine atoms, the wing components are separated by a distance of 380 Oe (Fig. 4*b*).

It is noteworthy that the intensity of the wing lines is almost ten times less than the intensity of the central components. The intensity of the wings of the lines is so low that, to a first approximation, one may assume that the spectrum of paramagnetic centres with one or two α-fluorine atoms consists of a relatively narrow singlet.

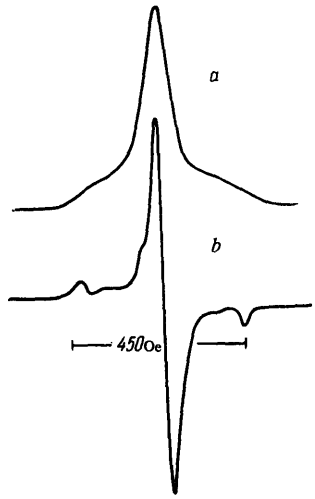
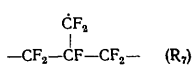


Figure 5. Absorption spectrum and its first derivative for the radicals $-CF_2-CF(\dot{C}F)_2-CF_2-$ at 77°K.

This impression, which arises from an analysis of the derivative of the absorption signals, is due to the characteristic line shape for each fluorocarbon radical. In the spectra of the radicals the overall spread of the absorption is very large but the derivative of the signal decreases fairly rapidly and significantly on passing outside the point corresponding to the maximum slope of the absorption signal. To illustrate these features of the spectra, Fig. 5 presents simultaneously the form of the absorption signal and its derivative for the radicals



(R_7)

in polycrystalline specimens.

IV. PARAMAGNETIC CENTRES IN IRRADIATED POLYTETRAFLUOROETHYLENE

The ESR spectra of irradiated polytetrafluoroethylene (PTFE) have been investigated in a number of studies[5-15]. As a result of radiation-chemical processes, as a rule several types of paramagnetic centres are formed in the irradiated polymers. The fluoroalkyl radicals

$$-CF_2-CF_2-\dot{C}F-CF_2-CF_2- \quad (R_8),$$

are formed in PTFE with a relatively large radiation yield. The ESR spectra of R_8 radicals at two temperatures obtained in two investigations[7,15] are presented in Fig. 6. At 523°K Lebedev et al.[7] observed hyperfine splitting in the spectrum of the R_8 radical due to interaction with four

γ-fluorine atoms (Fig. 6*a*). The γ-splitting is 3.5 Oe. At room temperatures the γ-components are not resolved.

It has been found in studies at room temperature[6] that the isotropic constant for the α-fluorine atom is 92 Oe and that for the β-fluorine atom is 33 Oe. Fig. 6*b* presents the spectrum of the R_8 radical at 77°K.[15] It is noteworthy that at this temperature components due to interaction with the β- and γ-fluorine atoms appear.

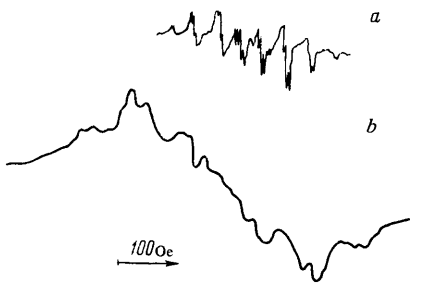
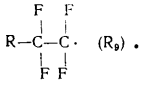


Figure 6. First derivative absorption spectra of the radical $-CF_2-CF_2-\dot{C}F-CF_2-\dot{C}F_2-$ at 523°K (curve *a*) and 77°K (curve *b*).

A relatively detailed study of R_8 radicals in PTFE was made for polymers partially oriented by extrusion[11]. It was observed that the width of the individual spectrum components is 9 Oe in cases where the H_0 field is perpendicular to the extrusion axis. When the H_0 field is parallel to the extrusion axis, the width of the component increases by a factor of two. The splitting by the α-fluorine atom is a minimum, amounting to 25 Oe, when the H_0 field is directed along the extrusion axis. It is noteworthy that the form of the spectrum for R_8 radicals at room temperature is determined to a considerable degree by isotropic interactions. The maximum splitting by the α-fluorine atom is only 92 Oe, although for the other fluorocarbon radicals with one or two α-fluorine atoms discussed previously the splitting at the same temperature is greater by a factor of two. This feature of the hyperfine interactions involving the α-fluorine atom at room temperature is somewhat obscure.

Ovenall[11] succeeded for the first time in detecting the terminal radicals



It was found that in the ESR spectra of PTFE specimens with the extrusion axis oriented parallel to the direction of the external field, wing components are observed, the centres of which are separated from each other by 390 Oe, the components having an additional triplet splitting of 25 Oe (Fig. 7). The paramagnetic centres responsible for these lateral components contribute to the central part of the overall spectrum. The observed spectrum may be attributed to the terminal R_9 radicals, since a splitting of 390 Oe can be produced only by two α-fluorine atoms. The triplet splitting of the wing components is due to the two β-fluorine atoms.

The ESR spectrum of the terminal R_9 radicals in polycrystalline specimens was observed for the first time by Bruk et al.[16] It has been shown[17] that the R_9 radicals are formed in irradiated PTFE and the reasons found why they could not be detected for a long time although their concentration is comparable to that of the R_8 fluoroalkyl radicals. The experimental results and spectroscopic considerations on the basis of which the R_9 spectra were identified are considered briefly below.

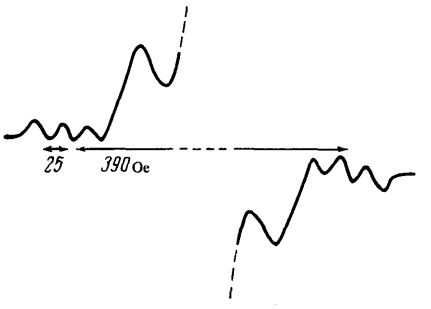


Figure 7. Lateral components of the first derivatives of the absorption signals of the radicals $R-CF_2-\dot{C}F_2$ on irradiation of oriented PTFE (extrusion axis parallel to H_0).

Irradiation of a frozen tetrafluoroethylene (TFE) monomer and secondary processes result in the formation of polymeric PTFE. After an irradiated tetrafluoroethylene specimen is heated to room temperature and the monomer is vaporised, the resulting polymer shows ESR spectra. The intensity of these spectra as well as the yield of the polymer depend on the irradiation temperature. A correlation between the intensity of the spectra and the yield of the polymer is observed also as a function of the radiation dose. As an illustration, Fig. 8 presents the spectra of tetrafluoroethylene specimens irradiated by an identical dose of 125 mrad at 98° and 128°K. It is seen that in the specimen irradiated at 98°K the overall concentration of radicals is higher than in the specimen irradiated at 128°K. After heating, the relative concentrations of paramagnetic centres change. Since the monomer was evaporated at room temperature, evidently the spectra in Figs. 8*b* and 8*d* are due to polymeric radicals.

The form of the spectra of these paramagnetic centres depends relatively little on temperature (Fig. 9). The average *g*-factor is 2.008.

We believe that the validity of the assignment of the spectrum in Fig. 9 to terminal polymeric radicals follows from the analysis of its form. The triplet spectrum may be accounted for by the presence of hyperfine interactions with the two β-fluorine atoms which in fact determine the splitting between the components, equal to 43 ± 1 Oe at room temperature. The splitting is consistent with the data obtained for single crystals in studies on the R_2 radicals; it was found that the isotropic constants for their β-fluorine atoms differ somewhat and are 34.5 and 40 Oe.

The absorption in the central part of the spectrum, where the triplet is in fact observed, is due to the R_9 radicals where the net nuclear spin of the two α-fluorine atoms is zero.

The R_9 spectrum does not show lateral components at a distance of 400 Oe characteristic of radicals with two

α-fluorine atoms. However, the presence in these paramagnetic centres of two α-fluorine atoms follows from the overall width of the spectrum. It is seen in Fig. 9*a* that the width of the absorption signal measured at a level of 0.1 of the maximum value is 300 Oe, while at a level of 0.02 it exceeds 450 Oe. We believe that such a large width of the spectrum can only be caused by the presence of two α-fluorine atoms.

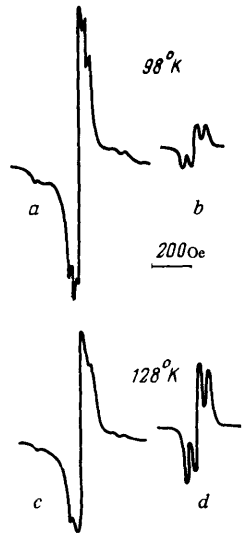


Figure 8. ESR spectra of tetrafluoroethylene irradiated at 98°K (curves *a* and *b*) and at 128°K (curves *c* and *d*). The spectra *a* and *c* were recorded at 77°K; the spectra *b* and *d* were obtained at 300°K after warming the specimens to room temperature.

We may note that recently a spectrum was obtained[19], which was attributed to R_9 radicals stabilised in a hydrocarbon matrix. In its central part it coincides with the spectrum in Fig. 9 and, moreover, it has wing components characteristic of two α-fluorine atoms.

In studies of irradiated copolymers of tetrafluoroethylene and hexafluoropropene (HFP) Iwasaki et al.[20,21], observed that, as a result of irradiation, the radicals

$$-CF_2-\dot{C}(CF_3)-CF_2- \quad (R_{10})$$

$$-CF_2-\dot{C}F-CF_2- \quad (R_{11})$$

are formed in the copolymer together with the R_8 radicals. The form of the spectra of the R_{10} radicals at 77°K and room temperature is presented in Fig. 10. The form of the absorption spectra and of the derivatives of the absorption spectra of the R_{11} radicals at 77°K is shown in Fig. 5.

As in the majority of other cases, the observed spectrum of the irradiated copolymer is due to the superposition of the spectra of paramagnetic centres of several types. Therefore the determination of the true form of the spectra of the R_{10} and R_{11} radicals and their identification presents certain difficulties.

It has been found[20] that the overall spectrum observed for the irradiated copolymer depends on the hexafluoropropene content. With increase of the concentration of hexafluoropropene, the form of the spectrum differs increasingly from the spectrum in TPFE. The authors attributed these spectral changes to the formation in the copolymer of new types of paramagnetic centres containing CF_3 groups.

By studying the dependence of the form of the spectra on the percentage content of hexafluoropropene and also the changes in the form of the overall spectrum as a result of heating the specimens, the authors[20] succeeded in obtaining the spectra of the individual types of paramagnetic centres by the method of graphical subtraction.

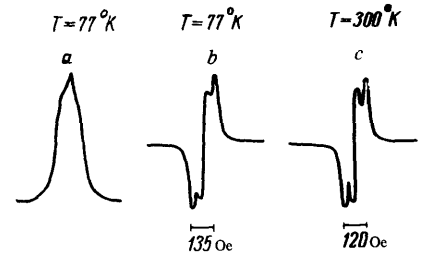


Figure 9. The absorption spectrum (*a*) and its derivatives for the $R-CF_2-CF_2$ radicals at 77° and 300°K (curves *b* and *c* respectively).

Oriented copolymers were prepared to identify the R_{10} radicals. It was found that the form of the spectrum in the copolymer at 77°K is almost independent of the orientation of the specimen in the magnetic field, while at room temperature relatively small spectral changes are observed. At the same time the form of the spectrum in oriented PTFE depends very significantly on orientation. Certain changes in the form of the spectrum as a function of the orientation of the specimen, which may be observed for the irradiated copolymer, can be accounted for by the superposition of the spectra of the R_8 radicals.

The anisotropy of the hyperfine coupling of β-fluorine atoms is known to be significantly less than the anisotropy for α-fluorine atoms[2,4]. The absence of an orientation dependence for the paramagnetic centres which disappear on heating shows that these cannot be α-fluorine atoms.

Using the isotropic hyperfine coupling constants for β-fluorine atoms, Iwasaki et al. constructed model spectra for the R_{10} radicals assuming that the form of the spectrum is due to the superposition of an unresolved isotropic hyperfine structure and obtained satisfactory agreement with the spectra of the paramagnetic centres which disappear on heating the copolymers.

The ESR spectrum of the R_{10} radicals at room temperature consists of weakly resolved components corresponding to the interaction with seven β-fluorine atoms, the splitting between adjacent components being 29 Oe.

At 77°K the R_{10} spectrum consists of a singlet line where the distance between the points of maximum slope is 80 Oe (Fig. 10*b*). It is noteworthy that, since R_{10} contains only β-fluorine atoms, the overall width of the spectrum changes only slightly as temperature is reduced. As a result of the different broadening of the R_8 and R_{10} spectra

over a range of temperatures due to the difference between the anisotropic hyperfine coupling constants, at 77°K the radicals R_{10} make the main contribution to the overall spectrum of the irradiated copolymer, while at room temperature the contribution by R_8 radicals is very significant.

It has been shown[21] that at 77°K and R_{10} radicals are converted into R_{11} radicals under the influence of ultraviolet radiation:

$$-CF_2-\dot{C}(CF_3)-CF_2- \xrightarrow[77^\circ K]{h\nu} -CF_2-CF(\dot{C}F_2)-CF_2- .$$

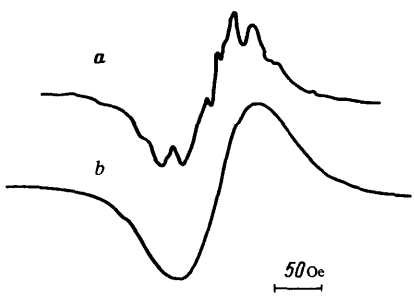


Figure 10. First derivative absorption spectra of the radicals $-CF_2-\dot{C}(CF_3)-CF_2-$ at 300°K (curve *a*) and 77°K (curve *b*).

The R_{11} radicals are stable only at low temperatures. At room temperature R_{11} is reconverted into R_{10}. The changes in the concentrations of R_{10} and R_{11} on ultraviolet irradiation at 77°K and on heating are reversible. The ESR spectrum of the R_{11} radicals has wing components, with a splitting of 450 Oe, characteristic of fluorocarbon radicals with two α-fluorine atoms. The R_{11} spectra were identified both by a comparison with the spectra of known radicals with two α-fluorine atoms, and by chemical considerations following from the reversible changes in the spectra as a result of heating or illumination.

When the copolymer is irradiated at 77°K the spectrum may be represented by the sum of the spectra of the R_8 and R_{11} radicals. On this basis, it was concluded[20] that at 77°K the most probable processes involve the following mechanisms:

a) copolymer $+\gamma \rightarrow \sim CF_2-CF(\dot{C}F_2)-CF_2\sim$;

b) copolymer $+\gamma \rightarrow \sim CF_2-\dot{C}F-CF_2\sim$.

V. PEROXY-RADICALS IN IRRADIATED POLYTETRAFLUOROETHYLENE

The radicals

$$-CF_2-\underset{\diagup\ \ \diagdown}{CF}-CF_2- \quad (R_{12})$$
$$\quad\ O-\dot{O}$$
$$-CF_2-CF_2-O-\dot{O} \quad (R_{13})$$
$$-CF_2-CF_2-\dot{O} \quad (R_{14})$$

have been detected[12] in irradiated PTFE. Until recently only the R_8 fluoroalkyl radicals could be detected in vacuum-irradiated PTFE. For this reason some investigators regarded the presence of R_{13} and R_{14} radicals in PTFE and the interpretation of the corresponding spectra as controversial[22,23].

The ESR spectra of the radicals R_{12}, R_{13}, and R_{14} at room temperature, obtained by Matsugashita and Shinohara[12], are presented in Fig. 11. Subsequent investigations[24] showed that the interpretation of these spectra is correct. However, bearing in mind that even in review articles[22,23] contradictory views are expressed, below we shall consider in detail the results, which confirm the validity of the suggested interpretation.

We believe that there are at least two reasons why the results of Matsugashita and Shinohara[12], which were obtained in 1961, are still controversial. Firstly the R_{12}, R_{13}, and R_{14} spectra of the individual types of paramagnetic centres were obtained by graphical subtraction and their interpretation was in many ways based on chemical considerations associated with the study of the reactions of the paramagnetic centres with various gases. The spectroscopic considerations based on the analysis of the line shape and g-factors were insufficient, although we believe that they were in fact correct.

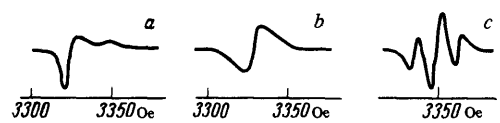


Figure 11. First derivative absorption spectra at 300° of the radicals $-CF_2-\underset{\diagup\ \ \diagdown}{CF}-CF_2$ (*a*), $\quad\ O-\dot{O}$ $-CF_2-CF_2-O-\dot{O}$ (*b*), and $-CF_2-CF_2-\dot{O}$ (*c*).

Secondly Matsugashita and Shinohara[12] failed to resolve the following important problem. According to their data the concentration of R_{13} radicals is comparable to the concentration of R_{12} and therefore it was necessary to postulate the presence of the radical $R-CF_2-\dot{C}F_2$ and the oxidation reaction

$$R-CF_2-\dot{C}F_2+O_2 \rightarrow R-CF_2-CF_2-O-\dot{O} . \quad (7)$$

However, neither Matsugashita and Shinohara nor other investigators were able to detect R_9 radicals in PTFE.

In the R_{12} and R_{13} radicals the unpaired electron is localised mainly in a molecular orbital involving the two oxygen atoms. In this connection it was not clear why at room temperature the R_{12} spectrum is significantly asymmetric, while the R_{13} spectrum is virtually symmetrical. It was also obscure why on irradiation of evacuated specimens containing only small traces of oxygen R_{14} radicals are observed and not R_{12} or R_{13}.

One of the important results associated with the study of the reactions with carbon monoxide was the observation of changes in the spectrum which were attributed[12] to the occurrence of the reaction

$$R-CF_2-O-\dot{O}+CO \rightarrow R-C\dot{F}_2-\dot{O}+CO_2 . \quad (8)$$

However, since there were doubts concerning the validity of the identification of both R_{13} and R_{14} radicals, the interpretation of the changes in the spectra after the introduction of carbon monoxide into the tube remained unconvincing.

According to Matsugashita and Shinohara[12], after oxygen has been admitted at a pressure of 100 mmHg into evacuated tubes containing PTFE irradiated at room temperature, the ESR spectrum of the peroxy-radicals formed is due to the superposition of the spectra of R_{12} and R_{13}.

When the same specimen is heated and re-evacuated at 423°K, it is possible to show by graphical subtraction that the radicals R_{12} disappear from the overall spectrum. On further heating and evacuation at 523°K, the spectrum due to R_{13} vanishes. As a result of heating, the R_{12} and R_{13} radicals disappear and the R_8 fluoroalkyl radicals reappear.

The average value of the g-factor of the R_{13} radicals is $g = 2.016$ and the width of the spectrum measured between the points of maximum slope is about 10 Oe.

Analysis of the width and intensity of the R_8 and R_{14} spectra shows that in evacuated PTFE specimens the concentration of R_{14} is almost one hundred times small than that of R_8. The possibility of detecting R_{14} radicals in a mixture with such values of the relative radical concentrations arises from the fact that the R_{14} radicals have a significantly narrower spectrum.

It is not altogether clear why, despite careful degassing of the polymer, R_{14} radicals are still detected in the specimens.

Iwasaki et al.[20] suggested that the principal chain of the polymer has units containing oxygen bridges:

$$\sim CF_2-CF_2-O-CF_2-CF_2\sim ,$$

the concentration of which is relatively high.

The dissociation of the C–O bond in these units in fact leads to the formation of R_{14}. We believe that this hypothesis is confirmed by the data of Barnaba et al.[24]

The ESR spectrum of R_{14} radicals is a triplet with a splitting of about 14 Oe between the components. The R_{14} radicals were identified on the basis that such triplet splitting is due to fluorine atoms. Since the splitting is small, the implication is that the unpaired electron density at the carbon atom linked to the fluorine atoms is low.

Indirect evidence supporting this interpretation comes from the spectral changes observed with specimen containing peroxy-radicals after the introduction of carbon monoxide. It was noted that the spectrum due to R_{13} disappeared and the intensity of the spectrum of the R_{14} radicals increased; this was explained by the occurrence of reaction (8).

The validity of the interpretation of the R_{13} and R_{14} spectra was confirmed in special experiments carried out by Barnaba et al.[24] in studies on paramagnetic centres in irradiated polytetrafluoroethylene oxide (PTFEO) polymers:

$$\sim O-CF_2-CF_2-O-CF_2-CF_2-O\sim .$$

Barnaba et al.[24] chose experimental conditions where predominantly either R_{13} or R_{14} radicals are detected in irradiated PTFEO. They succeeded in obtaining the spectra of R_{13} and R_{14} radicals using the different stabilities of these paramagnetic centres and in obviating the necessity of using graphical subtraction.

Additional evidence for the validity of the interpretation of the R_{13} and R_{14} spectra was based on the following experimental results. In the overall ESR spectrum recorded at 300°K directly after irradiation in a vacuum (at 273°K) of PTFEO specimens (Fig. 12) it proved possible to isolate the spectra of three types of paramagnetic centres. It was noted that, after treatment at 300°K for 24 h, the wing components of the spectrum of the specimen with a splitting of about 320 Oe disappeared.

Kinetic studies showed that the rate of disappearance of the outer components is the same as the rate of disappearance of one of the components contributing to the central part of the spectrum.

The splitting between the outer components (320 Oe) and the presence of lines associated with these paramagnetic centres in the central part of the spectrum show unambiguously that the mixture of paramagnetic centres includes radicals with two α-fluorine atoms. These centres are either

$$\sim O-\dot{C}F_2 \quad (R_{15})$$

or

$$\sim O-CF-\dot{C}F_2 \quad (R_{16}) .$$

Possibly both R_{15} and R_{16} are present in the specimens.

It is seen in Fig. 12*a* that the concentration of the terminal radicals (i.e. either R_{15} or R_{16}) exceeds the concentration of paramagnetic centres of other types. This follows from the fact that the spectra of the terminal radicals have the largest overall width and their intensities are comparable with those of the spectra of other types of paramagnetic centres.

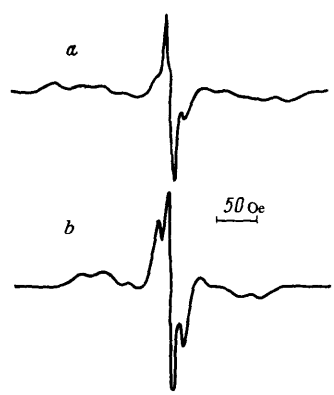


Figure 12. First derivative absorption spectra at 300°K of PTFEO irradiated in a vacuum at 273°K: *a*) immediately after irradiation; *b*) 24 h after irradiation.

After the destruction of the terminal radicals, two further types of paramagnetic centres remain in the specimen. The overall spectrum, corresponding to a particular ratio of the concentrations of these two paramagnetic centres, is presented in Fig. 12*b*.

The triplet spectrum, with a splitting between the components is 12.5 ± 1 Oe and contributing to the central part of the [overall] spectrum, was attributed to the R_{14} radicals.

The fact that the spectrum in Fig. 12*b* is due to the superposition of the spectra of two types of paramagnetic centres was proved by the authors using the different stabilities of these centres. During the storage of irradiated PTFEO in a vacuum at room temperature for several days, the intensity of the outer components (Fig. 12*b*) hardly changed, while the intensity of the central part was appreciably reduced. It was found that

after the admission of ethane to the specimen tube, these paramagnetic centres are destroyed at different rates; according to the authors, this also confirms the presence in the specimen of two types of paramagnetic centre.

In the spectrum in Fig. 12*b* the splitting between the centres of the outer wings is 180 Oe and the splitting within the wing components is 30 Oe. This shows that in the mixture there are paramagnetic centres with one α-fluorine atom and two β-fluorine atoms and therefore the authors reasonably suggested the presence of the radicals

$$\sim O-\dot{C}F-CF_2-O\sim \quad (R_{17}).$$

The relatively high stability of the radicals R_{17} in a vacuum confirms the validity of the suggested identification. The g-factor of the R_{14} radicals is virtually the same as the g-factor of diphenylpicrylhydrazyl (DPPH), which is 2.0036.

Directly after irradiation of PTFEO at 273°K, the concentration of terminal radicals is a maximum. This enabled Barnana et al.[24] to obtain the spectrum of the R_{13} radicals in a virtually pure form, which was found to coincide with the spectrum in Fig. 11 obtained by Matsugashita and Shinohara[12].

Barnaba et al. observed that after the admission of air to the PTFEO specimen irradiated in a vacuum, the reactions

$$R-\dot{C}F_2+O_2 \rightarrow R-CF_2-O-\dot{O}, \qquad (9)$$

$$\sim O-\dot{C}F-CF_2-O\sim + O_2 \rightarrow O-\underset{\displaystyle O-\dot{O}}{\overset{|}{C}}F-CF_2-O\sim \qquad (10)$$

take place. After the admission of air, the PTFEO spectrum is due to the superposition of the R_{12} and R_{13} spectra. When the PTFEO specimen irradiated in a vacuum is allowed to stand so that the concentration of terminal radicals in it is appreciably reduced, the R_{12} radicals make the principal contribution to the overall spectrum after the admission of air. On the other hand, when air is introduced directly after irradiation when the terminal radicals have the maximum concentration, the overall spectrum is due largely to the R_{13} radicals.

The ESR spectra of PTFE specimens irradiated in air are due to the R_{13} radicals. It was found that the R_{13} radicals are less stable at room temperature than R_{12}.

When the specimens are stored, the form of the overall spectrum is seen to change in accordance with the change in the concentration of the radicals R_{12} and R_{13}.

At room temperature the R_{13} concentration diminishes by a factor of two in the course of 100 h, while a similar change in the concentration of R_{12} requires 500 h.

Important evidence confirming the validity of the identification of the R_{13} spectrum is provided by the fact that Barnaba et al. detected the terminal R_9 radicals, showed that their concentration is greatest, and saw directly how the intensity of the ESR signal due to the R_{13} radicals increases by a factor of almost five as a result of reaction (7). The increase of signal intensity as a result of reaction (7) is associated with the fact that the R_{13} radicals have a significantly narrower ESR spectrum compared with that of R_9 and consequently at the same concentrations of paramagnetic centres the amplitude of the R_{13} signal is greater.

We believe that the work of Matsugashita and Shinohara[12] and Barnaba et al.[24] has shown that irradiated PTFE usually contains three types of peroxy-radicals. The present authors' results explained the reasons for the failure to detect the terminal radicals in PTFE.

It was found that the concentration of R_9 is comparable to the concentration of the R_8 fluoroalkyl radicals and that the R_9 radicals in PTFE at room temperature are relatively stable[17]. Therefore there is reason to believe that the R_{12}, R_{13}, and R_{14} spectra have been correctly identified.

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Qualitative Analysis in Gas Chromatography

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This review presents the most rational and widely employed methods of qualitative gas-chromatographic analysis of complex organic mixtures.
The bibliography includes 147 references.

I. INTRODUCTION

During the eighteen years of its development, gas–liquid chromatography has become one of the most widely used methods for the analysis of substances, in particular organic compounds. The greatest advances have been achieved using this method to separate complex mixtures of substances having low reactivity, the determination of which by other chemical and physicochemical methods involves considerable difficulties. For example, the problem of analysing petroleum fractions was solved by combining various chromatographic procedures. According to the latest data half the analyses of mixtures of organic substances in the U.S.A. are performed by gas chromatography and every seventh analytical chemist regards gas chromatography as his speciality. The comparatively simple equipment (available in many versions), the automatic recording of the results of separation, and the simple analytical procedure have attracted many investigators to gas-chromatographic methods. In the technological control of industrial processes this method is irreplaceable because of the ease with which the determination may be automated.

The advances in gas chromatography, as in all methods of separation, are associated primarily with the exceptionally high separating power of the chromatographic column. The high linear flow rate of the carrier gas and the small spreading of the chromatographic zone make it possible, in principle, to separate any mixture whose components differ, if only slightly, in their sorbability by the packing of the chromatographic column. However, for the analytical chemist it is important not only to separate the mixture into its components but also to evaluate the percentage present and in many cases also to determine their nature, i.e. to carry out qualitative and quantitative analyses. The methods for calculations on chromatograms, the estimation of the maximum accuracy of the chromatographic analysis, and the correlation of the readings of chromatographic detectors with the physicochemical properties of the substances separated are problems which have been successfully solved in many practical applications and here too no fundamental difficulties have been encountered.

The problems of qualitative analysis by gas-chromatographic methods have been investigated much less, although without a preliminary identification of the mixture components a complete quantitative analysis is impossible. It is paradoxical that in gas chromatography a situation has arisen where the final stage of analysis (the quantitative stage) has been developed to a higher degree than the first (the qualitative determination). Until recently hardly any attention was devoted to the problems of systematic identification of the components of the test mixture; the published data deal largely with specific problems.

The first stage of both qualitative and quantitative chromatographic analysis involves an attempt at the most complete separation of all the components of the test mixture. For such separation, use is made of a high-efficiency column preferably combined, with a programmed column temperature control during analysis. If it is known beforehand which components are present in the mixture, then for a qualitative analysis it is sufficient to employ a column which would yield a chromatogram with the number of peaks equal to the number of expected mixture components. In all other cases it is particularly desirable to employ temperature programming to detect the entire range of products. Only after it has been shown that all the components of the test mixture emerge from the column over a fairly short period, is it possible to abandon temperature programming and to employ isothermal analytical conditions. In order to obtain highly effective columns, capillary gas chromatography may be employed, but packed columns with lengths up to 50 m and having efficiencies equivalent to 50 000 theoretical plates have also been described[1]. In preliminary tests it is usually desirable to employ comparatively short packed chromatographic columns, 1–2 m in length, with temperature programming and only then to proceed to highly efficient columns to check the completeness of the separation of the mixture components. Satisfactory results are obtained when 2–3 high-efficiency columns (3–5 000 theoretical plates) with stationary phases of different types are employed. If there are no *a priori* reasons for a particular procedure, one chooses for qualitative analysis the columns which yielded the greatest number of peaks in preliminary tests. Usually columns with stationary phases of moderate or low polarity prove to be the most effective.

After a preliminary separation chromatogram has been obtained, it is necessary to make sure that each peak contains only one substance. For this purpose, the form of each peak in the chromatogram is analysed in the initial stage: a sharp distortion of peak symmetry and anomalous broadening of the bands are frequently indications of incomplete separation of the substances[2]. The most reliable results are obtained when each peak is collected in a trap and the eluate is subsequently separated on a column with a stationary phase of a markedly different type. Sometimes it is useful to treat the eluate chemically in order to obtain derivatives which can then be separated on the chromatographic column. However, in the separation of structural isomers and substances with similar physicochemical properties the above method may prove to be unsuccessful. To separate such isomers, use is made of selective sorbents or high-efficiency columns under isothermal conditions at several different temperatures.

The scheme for successive systematic qualitative analysis is as follows (see Scheme). The test mixture is

Scheme for systematic qualitative analysis by gas chromatography.

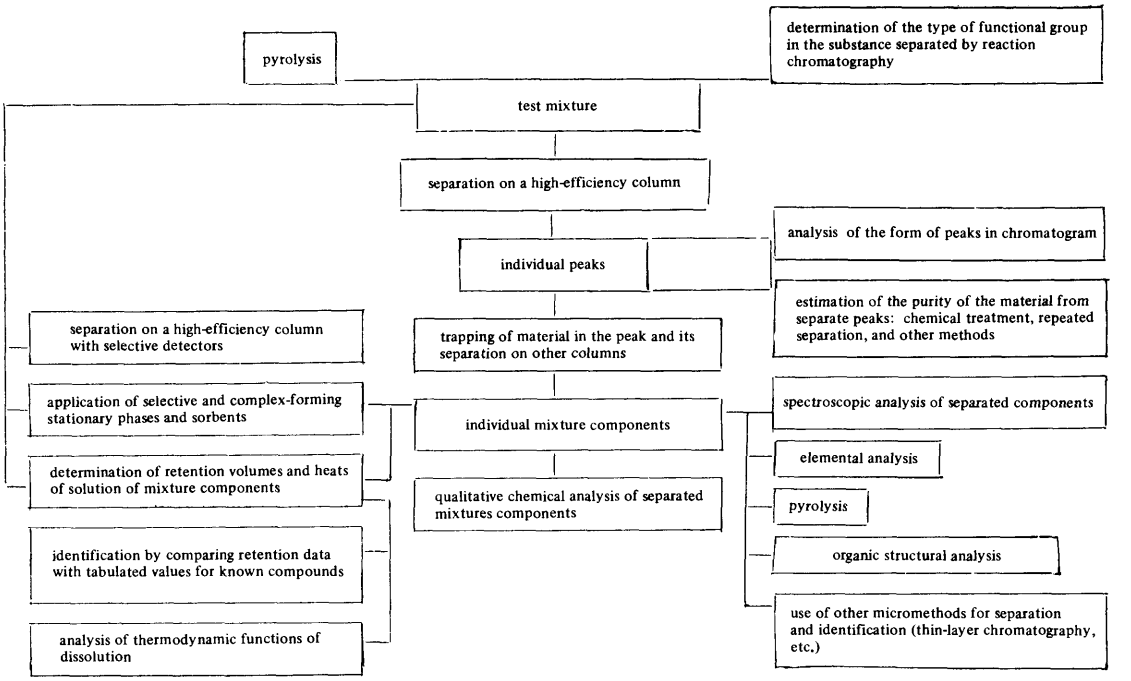

Table of principal methods for identification employed in qualitative gas-chromatographic analysis.

Method	Purpose and range of applicability	Advantages	Disadvantages
Use of stationary phases of different polarity and complex-forming sorbents	detection of individual structural groups and bonds in the molecule and overall estimation of polarity	simplicity of method (moderately laborious)	except when complex-forming sorbents are used, the method yields only approximate information about the polarity of the molecules
Reaction gas chromatography	determination of the functional groups of the compounds in initial mixture	does not require preliminary mixture separation	necessity for modifications of chromatographic apparatus. The functional groups and their position in the molecule are not always determined
Qualititative chemical analysis of separated substances	determination of the functional groups of the compounds after chromatographic separation	possibility of employing a large number of methods in the tests	necessity for complete separation of components investigated; sometimes comparatively large amounts of the substances are required
Organic structural analysis with chromatographic identifiaction of reaction products	determination of the carbon skeleton and the positions of the functional groups in the molecule	high reliability	necessity for the isolation of the pure substances. Laborious procedure
Pyrolysis	analysis of solid substances and high-boiling liquids	high sensitivity to slight changes in molecular structure	special aparatus and pure substances required
Comparison of the retention volumes and heats of solution of the test substances with data for known compounds	applicable to all compounds apart from pairs of isomers difficult or impossible to separate	simplicity of method (moderately laborious)	all the retention data for the substances whose presence is postulated in the mixture must be known or accurate relations for homologous series of these compounds are required
Analysis of thermodynamic functions of dissolution	applicable to all compounds; the molecular size and the number and positions of the functional groups are established	data for the retention of the substances whose presence in the mixture is postulated are not required	the use of semiempirical relations for the given chemical class of compounds; trained investigators needed
Selective detection	in the presence of C, O, Cl, and P atoms and of an aromatic ring in the compounds analysed	preliminary separation not required; high sensitivity	limited number of selectively determined characteristics of the molecules
Spectroscopic analytical methods	determination of the type of functional groups and their distribution and molecular size	extensive information about various molecular properties	need for the pure substances separated, sometimes in large amounts, complexity of the interpretation of the spectra, and the high cost of equipment
Elemental analysis	determination of the relative amounts of the elements in the substance separated	reliable information about elemental composition	need for special equipment and for the purity of the substances separated
Thin-layer and liquid chromatography, determination of physicochemical constants	identification on the basis of tabulated data for known substances	simplicity of method	neeed for the substances separated in pure form, sometimes large amounts; need for data for all the substances which may be present in the mixture

subjected to chemical reactions whereby it is possible to remove or transform chemically certain classes of compounds. Tests of this kind in combination with qualitative tests for functional groups of the separated substances collected in traps make it possible to assign the compounds to particular chemical classes and in many cases to obtain indications of the distribution of the functional groups in the molecule. When literature data are available on the retention of compounds in the same chemical classes as those detected in chemical tests, an attempt is made to compare the relative retention volumes and the heats of solution of the test substances with the tabulated data using 2–3 stationary phases of different types. If the test mixture contains components for which there are no published retention data and the postulated substances are not available in a pure form, then more complex methods of qualitative analysis are employed. The study of the thermodynamic functions of solutions in standard stationary phases makes it possible to elucidate the distribution of the functional groups in the molecule of the test compounds, the size of the molecule, and the structure of its carbon skeleton. The problems can also be solved with the aid of traditional methods of structural organic microanalysis and with the aid of various physicochemical procedures: infrared spectroscopy, mass spectrometry, nuclear magnetic resonance (NMR), determination of the melting and boiling points, and also in combination with other methods of separation, in particular thin-layer chromatography (see Table). Valuable information about the nature of the molecules of the components is provided by selective chromatographic detectors, elemental analysis, and pyrolytic gas chromatography. The main aim of this review is to describe various aspects of the application of these methods in qualitative analysis by gas chromatography.

II. APPLICATION OF QUALITATIVE CHEMICAL REACTIONS FOR THE DETERMINATION OF FUNCTIONAL GROUPS

The purpose of this method of identification in gas chromatography is to determine the type of functional groups in the test substance. Qualitative chemical reactions constitute the simplest and most reliable procedure for solving this problem [3] and such tests are possible both with the entire initial mixture and with the components separated. It is desirable to carry out the reactions with the initial mixture when all or the majority of the components are unknown. On the other hand, when only a few of the components are to be identified, it is more reasonable to establish the chemical nature of their functional groups by qualitative chemical tests on the separated substances.

The initial mixture is treated in reactors incorporated in the gas system of the chromatograph (less often) or functioning separately (more usual procedure). The first method requires a number of precautions in carrying out the reaction: the reaction time and the volume of the reactor must be sufficiently small so as not to affect the retention time or the form of the peaks for the substances separated and the reactor temperature chosen must be close to the temperature of the column or of the metering device. The stream of carrier gas is blown through the reactor during the entire period of the experiment and the chemical nature of the gas should promote the occurrence of the required reactions. In some cases, for example in hydrogenation reactions, the carrier gas must be pure hydrogen or its mixture with an inert gas. The design of the reactors not included in the gas system of the chromatograph can be of any kind. Such a reactor can consist of a tube with an outlet arm, which is closed by a self-sealing rubber system [4]. The outlet arm is connected to the chromatograph via a tap. Volatile reaction products are blown out via the outlet arm of the reactor into the column and the liquid products are collected with a syringe and introduced into the metering device of the chromatograph. The reactor incorporated in the gas circuit of the chromatograph usually consists of a metallic (less often glass) tube filled with a reagent and inserted between the metering device and the beginning of the chromatographic column.

Comparison of the composition of the initial mixture and the reaction products can be made most simply using two identical parallel columns in the same chromatograph with the reactor inserted before one of the columns. After evaporation and metering, the initial mixture is passed through a stream divider, which directs the two parts of the sample into the parallel columns; the ends of these columns are connected to the opposite chambers of the katharometer or differential flame-ionisation detector. In this scheme the pen recorder records only the peaks of the components which have fully or partially reacted, since the detector signals due to the unchanged peaks emerging simultaneously from the two columns cancel out. The reaction products and the composition of the initial mixture can be compared on different apparatus with the same columns. A partial decrease of the peak area of a particular mixture component indicates either that the reaction with the given substance is incomplete or that the peak contains two or more unseparated substances one of which has reacted with the reactor material. The disappearance of the peak is evidence that the substance has reacted with the substance in the reactor.

If the reaction yields volatile products (for example in the esterification of aliphatic acids), the retention data for the reaction products must be determined in order to identify them; an effort is made to select a type of chemical reaction which yields well known and readily available substances—for example hydrocarbons in exhaustive hydrogenation. If the reagent is volatile at the column temperature, then the need for a special reactor may be obviated, the reagent being introduced directly into the chromatographic column via the metering device before or immediately after the introduction of the test mixture. For example, alcohols may be acylated with acetic anhydride in this way.

The reaction with microamounts of substances can be carried out directly in the syringe needle, which is filled with Chromosorb for this purpose and the reaction mixture is then drawn in. After this the needle pierces the selfsealing rubber of the metering device, which is heated to the reaction temperature. The reaction reaches completion in several seconds and by moving the piston of the syringe the volatile products are forced into the chromatographic column where the substances are separated [5].

The methods of reaction gas chromatography enumerated above are based on the fact that they make it possible to compare the compositions of the reaction mixtures and the initial substances on various chromatographic columns. However, it is possible to modify the apparatus in such a way that a comparison may be made using the same chromatographic column with a flow divider [6]. The latter consists of a capillary passing through the reactor; part of the gas stream together with the unchanged components

of the initial mixture flow through this capillary into the chromatographic column. By altering the cross-section of the capillary, it is possible to regulate the amount of unreacted substance. Comparison of the chromatograms for mixture separation using different capillary cross-sections makes it possible to follow clearly the components whose amount decreases as the capillary diameter is reduced (there is a corresponding decrease in the amount of substance by-passing the reactor).

The reaction most widely used for qualitative analysis in gas chromatography is selective or exhaustive hydrogenation of the mixture components. The latter version permits group analysis in terms of the size and structure of the carbon skeleton of the molecule. The oxygen atoms in the test substance are reduced to water and other heteroatoms are either liberated in a free form or are reduced; exhaustive hydrogenation yields the saturated hydrocarbon corresponding to the carbon chain of the initial substance. If the heteroatoms are located between carbon atoms, then, after exhaustive hydrogenation, the corresponding molecular fragments are produced—a set of hydrocarbons the molecular sizes of which are determined by the size of the carbon radicals. In hydrogenation under gas-chromatographic conditions platinum [6,7], nickel [8], and palladium [9,10] catalysts are employed. The platinum catalyst operates at a relatively low temperature but it is also more sensitive to poisoning by sulphide and diene compounds. It is more convenient to carry out hydrogenation on a palladium catalyst in the temperature range between 150° and 260°C. Hydrogenation reactors are employed not only in combination with packed columns but also in combination with capillaries [11].

Reactions which remove particular classes of chemical compounds are most widely employed in the qualitative determination of unsaturated compounds in complex hydrocarbon mixtures. Olefins may be absorbed by a column containing silica gel impregnated with sulphuric acid [12,13] operated at temperatures between 20° and 50°C. In order to absorb ethylene and acetylene, which are not absorbed quantitatively by concentrated sulphuric acid, a solution of silver sulphate in sulphuric acid is employed. Sulphuric acid removes also aromatic compounds [14]. Apart from sulphuric acid, mercury perchlorate [15] and copper(II) chloride [16] are used to eliminate unsaturated compounds. Maleic anhydride absorbs butadiene [17,18].

Straight-chain alkanes are removed from mixtues by molecular sieves [19,20]. Alcohols react with boric or metaboric acids with formation of involatile compounds [3,21]. Aminoacids are converted by oxidation into volatile aldehydes, ninhydrin being employed for this purpose [22]. Reactors with phosphoric acid are used to decarboxylate aliphatic acids [23]. Aldehydes and ketones are removed with sodium bisulphite [24]. The same paper [24] describes a method for the elimination of sulphur-containing components in a reactor containing mercury(I) chloride. Secondary and tertiary alkylbromides are absorbed by silver nitrate [25] and amines by phosphoric acid [26]. Water vapour reacts with calcium carbide [27] and is retained in a reactor containing potassium carbonate [28].

Esterification is widely used in gas chromatography not only for quantitative analysis but also to convert reactive aliphatic acids into readily separated esters. For this purpose, the reaction is carried out between potassium salts of aliphatic acids and sodium ethyl sulphate [29,30] at 300°C or tetramethylammonium salts are pyrolysed [31]. Alcohols form esters with sodium nitrite [32,33] and with acid anhydrides [34]. Esters may be hydrolysed [35] with subsequent chromatographic determination of the products formed. The position of the double bond in the molecule of an unsaturated compound can be established by ozonolysis [36,37].

A very interesting version of qualitative reactions with the initial sample has been described [38]. This type of test is suitable for mixtures of substances the components of which do not boil above 200°C, since the entire mixture must be evaporated at room temperature in a closed vessel before the test. The gas from this vessel is drawn into a syringe on the walls of which the appropriate reactant has been deposited. After the reaction at room temperature the sample is introduced into the chromatograph by moving the piston of the syringe; the chromatogram indicates the composition of the test mixture after the chemical reactions in the syringe.

Much information about the functional groups of the components may be obtained using qualitative chemical reactions on the separated substances beyond the column, transferring them together with the carrier gas into appropriate reagents or collected in traps. The design of the traps depends on the aim of the experiments: universal traps are employed to condense components in amounts ranging from a fraction of a milligramme to 50 mg and special traps are designed where the condensed substance is subsequently subjected to a particular physicochemical determination, for example the recording of the infrared or mass spectrum. Simple glass U-traps attached to the chromatograph via a seal of heat-resistant rubber are normally used in qualitative analysis. To collect or remove very large amounts of the substance (in excess of 50 mg), various traps employed in comparative chromatography are used [39]. Such large amounts of selected separated substances may be needed in structural organic analysis, in the determination of the boiling and melting points, and in certain spectroscopic analyses. To achieve complete condensation of the separated components emerging from the column, it is necessary to create a turbulent gas stream and prevent an unduly high temperature gradient in the trap. The latter condition is particularly important to prevent the creation of a mist and therefore the use of liquid nitrogen and metallic traps is not recommended for the condensation of high-boiling compounds. Traps for semipreparative purposes may be used both at atmospheric and reduced [40] pressures.

The designs of traps for the collection of very small amounts of substance (down to 0.1 mg) has been described [41,42]. The trapping process in such traps takes place in two stages: initially the eluate is collected in a short section of the chromatographic column at a reduced temperature and then, on heating this section a slow stream of gas transfers the fraction collected into the microtrap. Traps for the collection of microamounts of substances which are simple but not really effective consist of the needle of a syringe or short Teflon capillaries [43] cooled with dry ice. For subsequent use, the condensate in such traps in washed off with a solvent or centrifuged.

A number of special traps have been constructed for subsequent employment in the measurement of infrared spectra. Some of them are first filled with a powder transparent to long-wavelength infrared radiation: potassium bromide or lithium fluoride. The products separated in the chromatographic column are condensed on the surface of these powders [44]. Traps where the condensation of the separated substances is achieved on the surface of a cellulose filter [45], which is then placed in an infrared spectrophotometer, have been described. Traps for the collection of very small amounts of separated sub-

stances are also used for the subsequent determination of the infrared spectra of the condensed substances [41,46]. In order to trap the substances for later determination of their mass spectra, traps with an adsorbent filler (molecular sieves, etc.) are used [47]. The substances emerging from the chromatograph are trapped by the sorbent in the cold, then the sorbent is transferred to a tube sealed to the filling system of the mass spectrometer. On heating, part of the substance is desorbed and passes into the mass spectrometer. Traps filled with powders transparent to infrared light have a low trapping efficiency, which may be enhanced by cooling the trap. Devices with adsorbents can be used only to trap relatively low-boiling substances, since desorption of high-boiling substances and substances with highly polar molecules requires high temperatures; there is then a real risk of the degradation or isomerisation of the adsorbed substance.

Qualitative reactions with the separated substances can be performed either directly in the trap or in a vessel after washing the substance out of the trap with a suitable solvent. The principal requirement which must be met in the application of reactions of this kind is high sensitivity (about 10–20 μg). The most suitable are drop reactions and methods specially tested in chromatographic practice [48].

The determination of the carbon skeleton of the separated compound constitutes a very important operation in qualitative chromatographic analysis. For this purpose, use is made of exhaustive hydrogenation on palladium and platinum catalysts [49–51] and attention is concentrated not on the rapidity of hydrogenation but on the completeness of the process and on the prevention of undesirable side reactions such as dehydrogenation and isomerisation. After separation in the chromatographic column, the substance collected in the trap is passed in a stream of hydrogen through the reactor (length about 24 cm), is again collected in a trap, and transferred for analysis on the chromatograph, where the resulting hydrocarbon is identified by its retention time. In those cases where it is very difficult to determine the particular isomer of the alkane formed, a methylene group is introduced [52]. In the analysis of the separated substance there is a possibility of establishing not only the presence of heteroatoms in the molecule but also, in a number of cases, the nature of the chemical bond between the heteroatom and other parts of the molecule, as has been done, for example, with nitrogen [53,54]. In particularly complex cases use may be made of the classical procedures of organic structural microanalysis.

III. THE USE OF RETENTION DATA ON VARIOUS STATIONARY PHASES AND ADSORBENTS

Certain preliminary information about the nature of the substances separated may be obtained by studying the retention of the mixture components on various stationary phases. Best results are obtained by this method in the determination of the retention volumes of substances which were first separated and collected in traps. On the other hand, when the experiments are performed with the entire initial mixture, it is necessary to separate the principal components, otherwise it is impossible to determine to which component particular retention data on various stationary phases refer.

Comparison of the relative retention volumes of the test substances (using a paraffin as a standard) reveals the relative polarities of their molecules [55,56]. If the test compound has polar or readily polarised functional groups (for example, C=O or C–Cl), then on transition from a non-polar to a polar stationary phase the relative retention volume increases. A quantitative estimate of the polarity of the given compound is obtained by measuring such increase. It should be recalled that the polarity of the component characterises only the general properties of the molecule but cannot serve for an unambiguous determination of its structure and the number and nature of the functional groups. Certain relations between molecular structure and the relative retention volumes on various stationary phases have been discussed in a monograph [55].

More definite information about the nature of the test substances is obtained using complex-forming stationary phases and sorbents. For a successful application of such methods, it is necessary that the mixture analysed contains substances which are selectively retained on the complex-forming sorbent. For example, alcohols and phenols are selectively retained on hydroxylated stationary phases. For selective retention of unsaturated compounds, use is made of stationary phases consisting of solutions of silver nitrate in polar liquids (ethylene glycol, benzyl cyanide, *p*-xylyl cyanide, etc.). These stationary phases are used to isolate ammonia [57], olefins [57–60], and other unsaturated hydrocarbons.

The high selectivity of certain adsorbents permits their use in determining the nature of the substances. For example, on silica gel and alumina unsaturated hydrocarbons are selectively separated from saturated hydrocarbons. Bentonites (complex-forming organic clays) with various additives have found the widest application. Isomers of xylene [61], dichlorobenzene [62], dimethoxybenzene, chloroacetophenone, and dimethylnaphthalene [63] are readily separated on these substances. Certain quaternary ammonium bases form complexes with π-donor molecules [64].

1. Identification by Comparing the Retention Data

After the establishment of the presence of particular functional groups in test substances, the compounds can be identified in terms of purely chromatographic quantities—the retention parameters. The retention characteristics are constant only for gas–liquid chromatography and therefore this type of identification is inapplicable to gas adsorption chromatography: in this case the retention volume depends not only on the nature of the compound separated but also on its amount (non-linearity of the adsorption isotherm). Retention parameters such as the relative retention volumes and heats of solution are most widely employed for identification. With the exception of the separation of polar substances on non-polar stationary phases, these quantities are virtually independent of concentration and the amount of the substance separated. If the result of the qualitative chemical reaction depends only on the nature of the functional group of the test compound, then solubility is a function of both the number of chemical groups in the molecule and of the size of the molecule and the structure of its carbon skeleton. Therefore agreement between the retention times of the test and standard compounds on the stationary phase does not constitute an unambiguous proof of their identity: usually in chromatographic practice one compares, for the purpose of identification, the retention volumes on three stationary phases of different types and, when the retention volumes and the relative heats of solution are determined, the

measurements are made on two stationary phases[55]. As a rule at least two liquids (a non-polar and a polar stationary phase) are employed.

For identification, it is most rational to employ relative retention data, since this entails a sharp improvement in the accuracy of the determination and of the agreement between the tabulated data of different authors. The limiting accuracy of the measurements of the relative retention volume is 0.2% and that of the relative molar heat of solution is 0.05 kcal; however, the scatter of the retention data of various authors may reach 5%. The choice of a suitable standard compound plays a major role, since the time required for its emergence must be reliably measured. For a better standardisation of data, it is recommended that the following standard substances be chosen for the measurement of the relative retention parameters: straight-chain alkanes (for non-polar stationary phases), benzene, and carbon tetrachloride; naphthane is suitable at high temperatures. The calculation of the relative retention volume with corrections for the experimental conditions and the determinations of the heats of solution from the temperature variation of the logarithm of the retention volume have been described in a monograph[55]. Identification by comparing the retention parameters can be achieved when pure samples of the substances postulated in the mixture are available (the best procedure) or on the basis of tabulated data[65-68].

If the test mixture is separated at an elevated column temperature, the retention characteristics of the components may be determined in a series of experiments under isothermal conditions with increasing column temperature: at each temperature the retention times are found for those components which are separated within a reasonable time. Then the logarithm of the retention volume is plotted against the reciprocal of the column temperature, the line is extrapolated to the chosen temperature, and the relative retention volumes of all the mixture components at a single temperature are determined from the table of antilogarithms. The determination of the retention volumes and heats of solution of the test substances in mixtures can be recommended only for simple samples containing several peaks of different size. In the general case more reliable results are obtained by collecting the separated substances in traps with subsequent determination of their retention parameters in columns with standard stationary phases.

In a number of studies compounds are identified by a comparison method using the retention indices, but these quantities have no advantages over the relative retention volumes and their use frequently leads to appreciable errors.

If there are no suitable tabulated data for the retention of the compounds thought to be present in the test mixture, it is possible to employ gas-chromatographic correlation methods. Such correlations hold best for the linear relation between the logarithms of the retention volumes of members of a homologous series and the number of carbon atoms in the molecule. The retention volumes for different stationary phases may be calculated by the method of linear correlations[69,70]. The slopes of the lines obtained by plotting the relative volumes for the test and standard substances along the ordinate axes are employed to determine the group to which the component belongs. Although the relation between the retention volumes of the substances separated in non-polar and weakly polar stationary phases and the boiling points has been investigated in a number of studies[70-74], a sufficiently reliable and universal correlation between these quantities has not been established. Such correlations hold only for a narrow range of substances of similar nature but even in optimum cases—solutions of hydrocarbons in hydrocarbon stationary phases—the error exceeds one degree. The boiling point and the logarithm of the retention volume can be unambiguously related only when the components separated and the stationary phase are of a similar type. The plotting of any kind of correlations for aromatic and other highly structured stationary phases, where the entropy factor and the steric hindrance to intermolecular interaction have a significant influence on the retention volume, should be avoided.

The procedure involving the use of various solvents to alter the solubility of the test substance, i.e. the method of determination of the quantity p is extremely promising[75]. The quantity p is the ratio of the solubilities of the test substance in a non-polar and a polar solvent, two immiscible solvents in the same vessel being employed. The values of p are measured for the test substances and then for the compounds whose presence in the mixture is suspected. Since all the measurements are made at room temperature and the choice of solvent is not governed by temperature limitations, it is possible to choose extremely selective solvents whereby the test compounds can be characterised fairly completely. The low temperature in the measurement of solubility favours the occurrence of specific and orientation interactions which make it possible to discover the fine structure of the test compound molecule. Since the amount of solute in each phase is determined chromatographically, the measurement of p is not very laborious. This method has been successfully used to identify isomeric compounds boiling at high temperatures[76-79]. The methods for the comparison of retention data require the availability of all the presumed components or their retention parameters. Certain linear correlations in homologous series may be employed for identification by a comparison method but for this one must be certain that the given test substance belongs to a particular homologous series. At the same time comparison methods have attracted investigators by their extreme simplicity and high reliability of the results. Therefore, when the experimenter has at his disposal the retention data for all the substances postulated in the mixture on 2–3 stationary phases, it is reasonable to employ the comparison method in combination with qualitative chemical analysis.

2. Analysis of the Thermodynamic Functions of Dissolution

If the use of qualitative reactions combined with a comparison of tabulated retention data cannot ensure a convincing identification, it is recommended that the method involving the analysis of the thermodynamic functions for the solution of the substances in standard stationary phases be employed[55]. This procedure has been used with particular success in those cases where there is no information about the substances postulated in the mixture and their physicochemical properties. This method of identification is perhaps simplest for the qualitative analysis of mixtures of polyfunctional compounds and high-boiling isomers, in particular hydrocarbons. An advantage of this procedure is less stringent requirements for the degree of separation of mixture components, since retention data can be determined also for incomplete separation of the components. The main principle of the thermodynamic method of identification consists in the calculation of the thermodynamic functions for the solution of the

postulated substances on the basis of the following characteristics of the molecules: molar refraction, van der Waals radii of the atoms and atomic groups, and the number of internal and external rotational degrees of freedom. The agreement between the calculated and experimental thermodynamic functions of the dissolution of substances in various stationary phases indicates a particular structure of the test substance molecule.

The semiempirical calculation of the heats of solution of various compounds in a non-polar stationary phase is simplest [80]. It is then possible to establish the size of the molecule and the structure of its carbon skeleton; the use of polar stationary phases provides evidence about the number and positions of polar functional groups in the molecule. Analysis of the entropy of solution permits conclusions concerning the rigidity of the molecular structure, the branching of the carbon skeleton, and the number of degrees of freedom associated with rotation—properties which characterise the molecule as a whole. The combination of qualitative chemical tests with the thermodynamic method of identification has been used to determine the products of various chemical reactions—oxidation of olefinic hydrocarbons [81,82], photochemical chlorination of olefins [83], and chlorination of acetone [84] and also for the determination of the composition of industrial mixtures [85].

Identification by the analysis of thermodynamic functions is the only method for the determination of the composition and structure of unknown compounds, particularly those for which no published data are available. However, such identification requires the availability of relations between the thermodynamic functions of solutions and molecular structure. Such relations hold for a fairly wide class of substances, but their use requires prior training of the investigator and a thorough knowledge of the nature of intermolecular forces. The application of this method for identification is possible only in combination with qualitative chemical tests for functional groups.

IV. APPLICATION OF SELECTIVE DETECTORS FOR IDENTIFICATION IN GAS CHROMATOGRAPHY

In a number of studies the high separating power of the gas-chromatographic column has been combined with the analysis of the fractions obtained on separation by infrared spectroscopic and mass-spectrometric measurements. The former provides information about the presence and location of the functional groups in the molecule and the latter about the size of the molecule. The combination of three types of apparatus—a chromatograph, an infrared spectrophotometer, and a mass spectrometer—permits the identification of up to 95% of all volatile organic compounds [1]. The optimum version of this device includes a high-efficiency chromatographic column [of the order of 50 000 theoretical plates] and a complex attachment for the interruption of the separation process during the determination of the spectra of the substances separated. The use of spectrometers as a means of identification imposes certain requirements on such devices: the capacity to record over a short period (3–10 min) the entire spectrum of the test substance and a very high sensitivity permitting the determination of the spectra of small amounts of the substances separated in the chromatographic column. The disadvantages of this combined apparatus include the necessity to interrupt the separation process during the recording of the spectrum and also the high cost of the spectroscopic devices.

One of the versions of apparatus of this kind involves the combination of a chromatograph with a cheap mass-spectrometer having a low resolving power which provides a continuous record for two mass numbers. An apparatus of this type has been called the "Khrommass". [86–88] The use of continuous recording of chromatograms in terms of the coordinates for various mass numbers permits the identification of the substance from the relative peak heights for various characteristic mass numbers [89], but this method becomes complicated with compounds containing more than five carbon atoms in the molecule. The combination of mass spectrometers with chromatographs allows the identification of a large number of compounds [90–92]. An undoubted advantage of the mass-spectrometric detector is its exceptionally high sensitivity, which permits its use in combination with capillary columns. A number of difficulties associated with the inertia of the mass spectrometer then arise; to eliminate this, short heated capillary junctions are employed between the chromatograph and the mass spectrometer [91,93–95] or the carrier gas is removed from the eluate [95,97]. However, the complexity of the design of the mass spectrometer and the need for highly trained operators for such apparatus limits its applicability in chromatographic practice. Reports have been published on attempts to employ radiofrequency mass spectrometers—the so called *QQ*-detectors [98]—but detectors of this kind have a low sensitivity and can be used to determine substances only up to a mass number of 250.

The application of ultraviolet spectrophotometry as a means of identification in gas chromatography is very limited, since its selectivity with respect to molecules having more than six carbon atoms is low, while such molecules in fact constitute the main bulk of the compounds separated by gas chromatography. The use of this method of identification for the analysis of xylene isomers has been described [99] and cases of the application of far ultraviolet absorption spectra in qualitative analysis have been noted [100,101].

The most sensitive selective spectroscopic detector is the flame photometric detector [102]. Its sensitivity exceeds by 1–2 powers of ten that of the flame-ionisation detector.

Two types of detectors, namely the electron capture and thermionic detectors, may be noted among the commonest detectors for qualitative analysis described recently. The operation of the first detector depends on the absorption of the slow electrons emitted by the radioactive source by the molecules of substances having positive electron affinities [103]. The detector signal depends on the capacity of the substance separated to capture electrons, which may be used as a valuable source of information about the properties of the test compound molecule, derived by comparing the chromatograms obtained using selective and non-selective detectors. All organic compounds may be divided into two classes in terms of their capacity to capture electrons: substances with simple capture and substances with capture by conjugated bonds. The first class includes halogeno-derivatives and the second conjugated aromatic systems. The presence of two and more electron-accepting atoms in the compound to be determined increases by 2–3 powers of ten the signal at the electron capture detector (ECD). This type of detector has been successfully used for the selective determination of halogeno-derivatives [104], polynuclear aromatic hydrocarbons [105], and steroids [103]. Since the sensitivity of the electron-capture detector towards substances having electronophilic groups is higher by several powers of ten than for other compounds, comparison of the chromato-

grams obtained using a universal detector and an electron capture detector determines unambiguously the properties of the test substance.

The thermoionic detector is extremely sensitive to chlorine- and phosphorus-containing compounds [106,107]. It is a modification of the flame-ionisation detector, into the flame of which a pellet compounded with an alkali metal salt is inserted. The conductivity of the hydrogen flame increases sharply only when chlorine- and phosphorus-containing compounds emerge from the column. The sensitivity of the thermionic detector is comparable to that of the flame-ionisation detector.

Halogen-containing substances are also determined by the Beilstein test performed visually [108,109] or automatically [101,110]. However, this test does not yield an unambiguous proof of the presence of a chlorine atom in the molecule, since many other compounds also give the same colour in the flame.

Detectors operating in conjugation with chemical reactions, for example automatic titrators, show the greatest selectivity with respect to a narrow range of compounds. The titrators determine selectivity free aliphatic acids [111] and sulphur-containing substances, which are converted into sulphur dioxide in the reactor beyond the chromatographic column [112]. Microcoulometric detectors for the selective detection of organosulphur compounds in complex mixtures have found wide application in the analysis of petroleums [113,114]. They have a very high sensitivity—down to 10^{-6} g of the substance.

A selective detector with a krypton-85 quinol lathrate evolves radioactive krypton on coming into contact with certain substances: chlorine, bromine, nitrogen dioxide, nitrogen oxychloride, and others [115]. This detector may be used for qualitative detection of halogens in the test compound after its combustion.

A detector operating on the principal of piezoelectric absorption can also be included among specific devices [116]. A vibrating quartz crystal is coated by a layer of liquid which absorbs selectively certain components of the mixture to be separated. The detector signal is proportional to the amount of substance absorbed by the liquid layer. The application of this detector is analogous to the use of two and more selective stationary phases for identification.

Detectors involving combustion on a platinum spiral have some selectivity [117,118]; their signal is proportional to the amount of heat evolved on combustion of the separated substance on the platinum spiral; by varying the temperature to which the platinum wire is heated, it is possible to alter the sensitivity of the detector with respect to various substances.

The molecular weight of the unknown substance may be determined by means of a detector the operation of which is based on the density of the gas (gas-density balance) [119-122]; it is applicable to substances with a not unduly high molecular weight—of the order of 100. The measurements are made with two different carrier gases; the main errors arise due to the inaccuracy of the measurements of the peak areas and the inconstancy of the composition of the standard mixture, amounting to about 5% in the most favourable cases. A more laborious method for the determination of molecular weight with the aid of a gas-density balance has been described [122]; in this case the error did not exceed 0.5%. The methods for the determination of molecular weight with a gas-density balance in gas chromatography have not found wide application, since they are suitable only at low column temperatures (the sensitivity of the detector falls rapidly as the temperature increases); on the other hand, the identification of low-boiling substances is not a difficult analytical problem.

Information about the number of carbon atoms in the test substance may be obtained with the aid of detectors involving the combustion of the separated substances to carbon dioxide [123,124]. The peak area is proportional to the number of carbon atoms in the molecule. When the peaks of the same substance in the mixture are compared first using a katharometer and then a device for its combustion, it is possible to estimate the number of carbon atoms in the molecule. Conversion of the separated products into methane, which is then detected by the katharometer, is employed to determine the number of carbon atoms in the molecule. The use of a detector which determines the amount of oxygen consumed in the combustion of the separated substances is very promising [125]. The amount of oxygen consumed is measured by the current necessary to produce this gas by the electrolysis of water. Analysis of the chromatograms obtained with such a detector permits the determination of the number of carbon atoms in the molecule which are not linked to oxygen atoms.

The use of selective detectors makes it possible to elucidate a number of specific properties of the substances separated—the presence of heteroatoms and certain functional groups and the number of carbon, hydrogen, and oxygen atoms in the molecule. Although spectroscopic detectors yield much information about the properties of the molecule, simple selective detectors have found wide application by virtue of their cheapness, simplicity of operation, and high sensitivity in the continuous recording of the results of separation. A disadvantage of selective detectors is high sensitivity for limited classes of compounds only. If the qualitative analysis is carried out in the laboratory fairly frequently, it is desirable to employ spectroscopic devices for identification. In the qualitative analysis of very small amounts of substances, only selective detectors and a mass spectrometer may be employed.

V. THE USE OF OTHER PHYSICOCHEMICAL METHODS FOR THE INVESTIGATION OF SEPARATED SUBSTANCES

In many cases qualitative analysis in gas chromatography is carried out with the aid of other physicochemical methods, for example thin-layer chromatography. Preliminary separation of very complex mixtures is frequently performed in the analysis of petroleum fractions, which involves liquid-adsorption chromatography. The fractions obtained are analysed by gas-chromatography. The converse procedure is also employed: the substances separated on a gas-chromatographic column are deposited on the starting line of the thin-layer chromatographic plate which moves at a constant rate relative to the output from the detector [126-128]. The separated substances are adsorbed on silica gel along the starting line, their positions on the line corresponding to the positions of the peaks on the chromatogram recorded by the katharometer. The chromatograms on the plate are then developed and the R_f values of the spots are determined. The identification is based on the R_f values for silica gel. The principal advantage of this method is its combination of the separation of the substances in terms of the form and size of the molecules by a non-polar stationary phase and in terms of the characteristics of the molecular structure

and the presence of functional groups by silica gel. The system obtained has an exceptionally high separating capacity. A certain disadvantage of the method consists in the fact that thin-layer chromatography requires a relatively large sample, which necessitates the operation of the gas-chromatographic column under conditions of overloading.

The substances separated chromatographically may be investigated by any micromethod. It is possible to determine their boiling and melting points by a micromethod [129] and to record and analyse the NMR spectrum [130]. These methods require a comparatively large amount of the substance (up to 100 mg), which presents certain difficulties, particularly in those cases where the relevant substance is present in the mixture in small amounts. It is somewhat more convenient to investigate the form and colour of the crystals under the microscope—the crystal may be the separated pure substances or the products of their chemical reactions [131]. The microscopic method for the investigation of crystal form makes it possible to distinguish the components of non-separated mixtures provided that they form crystals of different shapes.

Auxiliary physicochemical methods are comparatively rarely required for qualitative analysis in gas chromatography, since they are not very sensitive and universal.

VI. ELEMENTAL ANALYSIS

An additional source of information about the test substance is elemental analysis—this procedure is carried out by classical micromethods with the pure separated compounds collected in traps. The use of gas chromatography in elemental analysis makes it possible to reduce greatly the amount of labour required and to improve the accuracy of the experiments. The high separating capacity of chromatographic columns permits the determination of several elements in one operation. The first stage of elemental analysis in organic chemistry has remained unchanged and is based on the principle of the oxidation or pyrolysis reactions, but gas chromatography allows the use of extremely small amounts of the substances. Two versions of elemental analysis by chromatographic methods are possible: these involve a combination of the apparatus for the decomposition of the substance with a gas chromatograph or the separate operation of these devices with transfer of the reaction products to the chromatograph.

The combined device for the simultaneous determination of carbon, nitrogen, and sulphur consists of a reactor where the specimen is oxidised over copper(II) oxide in a stream of helium at 850°C and a chromatograph [132]. The reaction products (nitrogen, carbon dioxide, and sulphur dioxide) are separated at room temperature on a 1 m chromatographic column filled with Chromosorb P impregnated by 33% DS-550 silicone oil. The time required for the complete separation of the mixture is 4 min and the error of the analysis is 0.3%. If there is no need to determine sulphur, the substances are combusted on a mixture of copper(II) oxide and manganese dioxide at 600°C and the duration of separation is reduced to 1.5 min. Similar devices are used for the simultaneous determination of carbon, nitrogen, and hydrogen [133]; the water formed on combustion reacts with calcium carbide and is determined from the size of the acetylene peak. A mixture of nitrogen, acetylene, and carbon dioxide has been separated on a column containing 5 Å molecular sieves with a programmed temperature change from room temperature to 400°C at a rate of 6 deg min^{-1}. The duration of the complete analysis is 50 min.

Nitrogen and oxygen are determined simultaneously in the pyrolysis of the test substance over "nickel-plated" carbon black at 900°C. [132] The pyrolysis is carried out in the flame of a gas burner over a period of 5 min, the reaction products being separated at room temperature in a 60 cm column with a 5 Å molecular sieve. The analytical error is not greater than 0.8% and the total time required for the determination is 15 min. In all these methods the substance is decomposed in a stream of carrier gas and the outlet from the reactor is connected throughout to the initial section of the chromatographic column. The reaction products are immediately transferred by the stream of carrier gas to the column. The disadvantages of this method include the impossibility of employing oxygen for combustion and the spreading of the chromatographic zone during the finite period of the decomposition of the substance.

The subdivision of chromatographic elemental analysis into two stages makes it possible, at the expense of a slight increase in the analysis time, to separate the chromatograph from the reactor and to employ any conditions for the decomposition of the test substances. The reaction products are collected in a trap whence they are transferred to the chromatograph for analysis. This method for the determination of carbon and hydrogen in organic compounds has been described by Duswalt and Brandt [134]. The test substance is combusted in a stream of oxygen at a reactor temperature of 750°C over silvered copper needles, copper(II) oxide, and platinum, moisture being converted into acetylene by reaction with calcium carbide; carbon dioxide and acetylene condense in a trap and are then separated in a 90 cm silica gel column. The overall duration of analysis is 20 min and the absolute error is 0.5% with respect to carbon and 0.1% with respect to hydrogen. Similar results were obtained also in other investigations [135,136] with a slight modification of the conditions. By combining a gas-density balance as a detector with combustion of the products it is possible to determine the ratio of hydrogen and carbon atoms in the molecule [137]. However, the complexity of the apparatus in this method is not justified by the amount of information obtained with its aid.

By depositing alkali on an inert carrier, one can determine the number of Si–H groups in the molecule from the amount of hydrogen evolved on hydrolysis [138].

Catalytic hydrogenation of the separated substance at 1000°C leads to its complete conversion into methane [139]. The size of the methane peak after such hydrogenation indicates the number of carbon atoms in the molecule of the test substance. Catalytic hydrogenation of nitrogen-containing substances over nickel or magnesium oxide catalysts yields ammonia, the amount of which can be measured chemically or chromatographically [140].

Elemental chromatographic analysis is one of the auxiliary procedures for identification but it yields only the proportions of the elements in the test substance. The structure of the molecule and the location of functional groups in it are determined by other methods, described above.

VII. PYROLYSIS

One of the new trends in the gas-chromatographic identification of compounds is the use of pyrolytic gas chromatography. The pyrolysis is carried out in special cells

(with the amount of test substance between 0.1 and 1 mg) on a platinum wire or a ferromagnetic material, which may be convered by glass. The pyrolysis temperatures lie between 400° and 1200°C. The pyrolysis is usually performed to identify a single substance and more rarely a binary mixture. Pyrolytic chromatography can be most usefully employed for the identification of high-boiling compounds. Solid substances, in particular polymeric compounds, may be identified by this procedure. The pyrolysis products are carried by the carrier gas directly from the pyrolyser to the chromatographic column, where they are separated. The pyrolysis temperature is chosen in such a way that a number of peaks characteristic of the given compound are obtained on the chromatogram. Then the pyrolysis chromatograms of the unknown and known compounds are compared. The identity of the pyrolysis chromatograms is evidence of the identity of the substances compared. The method is the only one available for the identification of high-boiling compounds having isomers with similar properties. Such isomers are extremely difficult to separate on a chromatographic column at a high temperature, since the selectivity of stationary phases falls as the temperature increases. With a correct choice of reaction conditions, pyrolysis chromatograms are characteristic of a given compound [141-143]. The maintenance of rigorous constancy and reproducibility of the pyrolysis temperature is exceptionally important for identification, since the composition of the pyrolysis products varies as a function of reactor temperature. The study of the pyrolysis products at different process temperatures also helps characterise a pure substance. The pyrolytic method has proved extremely effective for the determination of impurities in solids, for example in the analysis of many substances in the living cell [144-147].

In conclusion we must consider the most rational methods for the identification of substances present in the mixture in different proportions. For substances whose concentration in the mixture is from 1% upwards, all the methods described above are applicable in principle, up to structural analysis by methods of organic chemistry. On the other hand, if it is necessary to identify impurity components, two procedures are suitable. The first consists in the concentration of the impurities by chemical or physicochemical methods. The concentrate is then analysed by the usual procedures. On the other hand, if such concentration is impossible, the following methods are employed for identification: selective removal or conversion of the mixture components in reactors, comparison of retention data, and thermodynamic analysis of the properties of the solution. Definite information is provided by mass spectrometers and selective detectors.

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Non-empirical Calculations of the Force Constants for Small Molecules

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The review gives a consistent description and analysis of the ideas underlying the determination of potential constants (coefficients of the potential function formulated as a power series in terms of generalised coordinates) for diatomic and simple monatomic molecules using quantum-chemical methods. Calculations for specific molecules of greatest interest both theoretically and practically are briefly considered; the results of these calculations are presented in the form of tables.
The bibliography includes 80 references.

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I. INTRODUCTION

The review deals with the present state of the solution of the problem of evaluation of a potential function of the type

$$V = \frac{1}{2!}\sum_{\alpha,\beta} K_{\alpha\beta} q_\alpha q_\beta + \frac{1}{3!}\sum_{\alpha,\beta,\gamma} K_{\alpha\beta\gamma} q_\alpha q_\beta q_\gamma + \frac{1}{4!}\sum_{\alpha,\beta,\gamma,\delta} K_{\alpha\beta\gamma\delta} q_\alpha q_\beta q_\gamma q_\delta + \cdots \quad (1)$$

where $K_{\alpha\beta}$ are harmonic (quadratic) molecular force constants, $K_{\alpha\beta\gamma}$ and $K_{\alpha\beta\gamma\delta}$ are anharmonic (cubic and quadratic respectively) force constants, and q_α are generalised coordinates.

The determination of force constants by the solution of the vibrational–rotational problem involves a fundamental difficulty—the number of unknowns is greater in the majority of cases than the number of equations which may be formulated from the available experimental data.

Therefore the approach based on solving the electronic problem in the adiabatic approximation [1], according to which

$$K_{\alpha\beta} = \left(\frac{\partial^2 E}{\partial q_\alpha \partial q_\beta}\right)_e,\quad K_{\alpha\beta\gamma} = \left(\frac{\partial^3 E}{\partial q_\alpha \partial q_\beta \partial q_\gamma}\right)_e,\quad K_{\alpha\beta\gamma\delta} = \left(\frac{\partial^4 E}{\partial q_\alpha \partial q_\beta \partial q_\gamma \partial q_\delta}\right)_e, \quad (2)$$

is of undoubted interest in connection with the possibility, in principle, of eliminating the above difficulty and also the possibility of achieving a deeper understanding of the nature of dynamic interactions in molecules.

At the present time the principal aim is of course to develop methods for the calculation of force constants and to test their effectiveness on comparatively simple systems, not merely to secure new data for the force constants of specific molecules.

Thus in Eqn. (2) E is the total energy of a molecular system containing N nuclei with charges $Z_1, \ldots, Z_N$ and n electrons†:

$$E = E_e + E_N, \quad (3)$$

where

$$E_e = \langle \Psi_1 H_e \Psi \rangle \quad (4)$$

is the energy of the electronic shells in the field of nuclei with the given configuration and

$$E_N = \sum_{\alpha>\beta} \frac{Z_\alpha Z_\beta}{R_{\alpha\beta}} \quad (5)$$

is the energy of the electrostatic interaction of the nuclei, excluding the kinetic energy of the motion of the latter.

In Eqns. (4) and (5), $\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_n; \mathbf{R}_1, \ldots, \mathbf{R}_N)$ is the electronic wave function and H_e is the electronic Hamiltonian:

$$H_e = \sum_{i=1}^{n}\left(-\frac{1}{2}\Delta_i - \sum_\alpha \frac{Z_\alpha}{r_{i\alpha}}\right) + \frac{1}{2}\sum_{i\neq j}\frac{1}{r_{ij}}\ ; \quad (6)$$

$R_{\alpha\beta} = |\mathbf{R}_\alpha - \mathbf{R}_\beta|$ is the distance between the nuclei α and β, $r_{\alpha i} = |\mathbf{R}_\alpha - \mathbf{r}_i|$ the distance between the ith electron and the α nucleus, and $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ the distance between the ith and jth electrons, the nuclear configuration being described by the vectors $\mathbf{R}_1, \ldots, \mathbf{R}_N$ and the electron configuration by $\mathbf{r}_1, \ldots, \mathbf{r}_n$.

In the adiabatic approximation function (3) plays the role of a potential energy V of the relative atomic vibrations employed in the theory of molecular vibrations [3]. Thus at equilibrium the total energy may be represented by the series (1) and the problem of determining the force constants of the molecule in the given electronic state now reduces to the calculation of the derivatives of the total energy of the system with respect to generalised coordinates.

II. NUMERICAL METHODS FOR THE CALCULATION OF FORCE CONSTANTS

We shall consider initially the possibilities which arise in the solution of the problem of the Hartree–Fock–Roothaan self-consistent field (SCF) method [4,5]. The applications and discussion of various aspects of the self-consistent field method in the calculation of other properties of atoms and molecules may be found in Sokolov's review [6].

Using the Hartree–Fock method, a number of investigators have calculated the electronic energy for various nuclear configurations (in the vicinity of the equilibrium configuration) for diatomic and small polyatomic molecules. Such calculations make it possible to plot potential curves and surfaces and to determine the potential constants by numerical differentiation. It must be emphasised that more calculations of this kind, particularly recently, became possible with increased availability of computers.

A typical example of such an approach, usually referred to in the literature as "traditional", is the calculation of

†The formulae and the numerical results in the review are quoted in atomic units (a.u.), unless otherwise stated [2].

the force constants of diatomic molecules in the ground and excited states by Fraga and Ransil [7] carried out on the basis of the self-consistent field functions in both the one-determinant approximation and taking into account the interaction between the configurations (CI).

In their studies the potential curve is approximated by a third degree polynomial in R of the form

$$E = a + bR + cR^2 + dR^3, \quad (7)$$

the coefficients of which are determined by the least square solution of a set of equations of the type of Eqn. (7) for various values of R and the corresponding E. Since the expressions for the vibrational–rotational constants (ω_e, $\omega_e x_e$, B_e, α_e, and $K_{\alpha\beta}$) can be obtained by solving the corresponding Schrödinger equation with a potential function of the type [8]

$$E = a - fR^2 - gR^3, \quad (8)$$

Fraga and Ransil converted the coefficients of Eqn. (7) into those of Eqn. (8) by the formulae $g = -d$ and $f = (c^2 - 3bd)^{1/2}$. This numerical analysis of the potential curves does not differ in principle from that employed in the majority of investigations. The only difference lies either in the choice of the approximating function or in the method of estimation of the similarity of the functions over a certain interval, etc.

The agreement between the $K_{\alpha\beta}$ calculated in the one-determinant approximation and the experimental values [8] is satisfactory despite the fact that the molecular orbitals (MO) include only the internal and Slater valence atomic orbitals (AO) and the polynomial (7) is restricted to the third power of R (Table 1); the deviations from the experimental values lie in the range 8–20% for the molecules H_2, LiH, and Li_2.

An interesting result was obtained by Nesbet in Hartree–Fock calculations for a number of diatomic molecules [9,10]; an appreciable improvement in the calculation of the force constants in the one-configurational approximation arises when polarisation and deformation of atomic orbitals as a consequence of their intramolecular environment are postulated, in contrast to the hypothesis that the molecular orbitals may be constructed as linear combinations (LC) of undeformed atomic orbitals. This effect may be described by including a greater number of basis functions than in the minimum set, with higher angular quantum numbers than for separated atoms.

To illustrate this, we shall quote the results of this type of calculation for the $^1\Sigma^+$ states of the isoelectronic molecules N_2, CO, and BF carried out by Nesbet [11]; in this case the potential curve is approximated by a series in terms of Chebyshev functions.

Then the analytical expression obtained for the potential curve can be put in the form

$$E = b_0\xi^2 \sum_k b_k \xi^k, \quad (9)$$

where $\xi = (R - R_e)/R_e$. Dunham [12] solved the vibrational–rotational Schrödinger equation with a potential defined by an expression of type (9). This makes it possible to find, using the formulae obtained, all the fundamental spectroscopic constants for a given bound state. Such numerical analysis of the potential curve is usually referred to as the Dunham analysis.

Table 1 shows that there is significant agreement with the experimental force constants. For N_2 as an example, it is seen that the constant $K_{\alpha\beta}$ is somewhat improved compared with the values calculated with the aid of the minimal basal set.

Satisfactory agreement with experiment was obtained also for the F_2 molecule by Wahl [13], who likewise employed the Hartree–Fock–Roothaan procedure in the derivation of the potential curve with subsequent Dunham analysis leading to the force constants. It should be noted that this study is the first in a series designed by the author and his coworkers to obtain Hartree–Fock analytical wave functions for the ground and certain excited states of diatomic molecules. They believe that the calculations should provide a foundation for a critical analysis of the theory of electronic structures of small molecules. Thus the third paper [14] of this series presents the calculations of the wave functions of N_2^+ and N_2 in the ground and excited states with various forms of basis sets. All the calculations were made for a large number of internuclear distances, which makes it possible to calculate the force constants (Table 1). To eliminate computational errors, several polynomial approximations were made varying the number (from 4 to 10) and type of points [15] taken for the Hartree potential curve. The discrepancies between the calculated spectroscopic constants and experiment range from several per cent to several tens per cent and those for the force constant are in the range 34–64%.

Comparison of the potential curves with experiment, carried out in the above investigations and in the work of Leies [16] for the H_2 molecule (the calculation was based on the Hartree–Fock function obtained by Kolos and Roothaan [17]), suggests [18] that the curves are relatively congruent in the vicinity of equilibrium (and when $R < R_e$); the difference in their behaviour increases at larger internuclear distances. In turn, the results of the calculations for the force constants and certain other vibrational–rotational constants are fully consistent with the form of the potential curves. Thus the Hartree–Fock potential increases more rapidly from the point of equilibrium ($K_{\alpha\beta}$ >) but shows a smaller anharmonicity ($\omega_e x_e$ <) than the experimental potential. Such behaviour of the Hartree–Fock potential curves is evidently due to the following factors: the Hartree–Fock molecular orbitals lead to an incorrect dissociation limit for the majority of molecules, i.e. the molecules dissociate to give a series of neutral and ionic atomic states; moreover, the Hartree–Fock potential does not include the correlation energy, which is partly the reason for the effect described above.

Yoshimine [20] shows that, from the standpoint of these factors, the introduction of a scale factor into the wave function and its variation as a function of R to improve the force constants [19] is not particularly useful [although the appropriate variation of the scale factors does in fact alter these constants in the required direction, the change is only slight (Table 1)]. Huo's use of even more extended sets [21] (CO and BF molecules), compared with the basis sets [11], and the optimisation of the scale factors does not lead to a significant improvement of the force constants.

Before proceeding to studies in which attempts were made to improve the E_{H-F}, mention should be made of a very interesting study by Goodisman [22], who showed that the force curve (obtained directly from the expectation value of the one-electron operator $\partial H/\partial R$) leads to better results for $K_{\alpha\beta}$ than the energy curve calculated on the basis of Hartree–Fock functions with limited-basis of functions of the James and Coolidge type, namely the approximation of the energy curve by a parabola in the vicinity of R_e yields the force constant $K_{\alpha\beta} = 0.3795$ a.u. and the calculated values $R_e = 1.385$ a.u. and $\omega_e = 4458\ cm^{-1}$; numerical analysis of the force curve gives $K_{\alpha\beta} = 0.3727$ a.u., $R_e = 1.394$ a.u., and $\omega_e = 4417\ cm^{-1}$

Table 1. Force constants of molecules.

Molecule	Method of calculation of f.c.	Force constants (f.c.), a.u. quadratic theor.	quadratic expt *	cubic theor.	cubic expt	quartic theor.	quartic expt	Refs.
H_2^+	numerical	0.0987[a]	0.1006	—	—	—	—	7
He_2^+		0.2835	0.2005	—	—	—	—	7
H_3		0.4091	0.369	—	—	—	—	7
H_2		0.3994	—	—	—	—	—	16
H_2		0.3968[a] 0.3387[c] 0.3689[d]	—	—	—	—	—	28
LiH		0.0771[a]	0.0659	—	—	—	—	7
LiH		0.048[e]	—	—	—	—	—	29
Li_2		0.0121[a] 0.0135[c] 0.0136[d]	0.0141	—	—	—	—	28
Li_2		0.0151[a]	—	—	—	—	—	7
B_2		0.3042	0.2260	—	—	—	—	33
HF		0.9237[a]	0.6204	—	—	—	—	7
HF		0.6809[b]	—	—	—	—	—	7
N_2^+		1.634[a]	1.291	—	—	—	—	7
N_2^+		1.751[b]	—	−2.135	−1.819	1.922	1.580[z]	14
N_2		2.340[a]	1.474	—	—	—	—	7
N_2		1.964[f]	—	—	—	—	—	11
N_2		1.974[b]	—	−2.964	−2.012	4.279	1.792[z]	14
CO		1.442	1.222	—	—	—	—	11
CO		1.533[g]	—	—	—	—	—	21
BF		0.496	0.518	—	—	—	—	11
BF		0.590	—	—	—	—	—	21
BH		0.300[b]	0.195	—	—	—	—	31
CO		1.353[a] 1.070[b]	—	—	—	—	—	26
LiF		0.2225[h]	0.1800	—	—	—	—	19
		0.2223[i]	—	—	—	—	—	
BeO		0.6598[h]	0.6200	—	—	—	—	20
		0.6598[i]	—	—	—	—	—	
C_2		0.513[b]	0.782	—	—	—	—	32
F_2		0.927[a] 0.511[b]	0.304	—	—	—	—	7
F_2		0.538[b]		−0.696	−0.435	0.566	0.345[z]	13
F_2		0.6047[a] 0.1652[c]	—	—	—	—	—	28
H_3		K_{R_1}=0.288[b]	—	—	—	—	—	31
		K_{R_2}=0.023	—	—	—	—	—	
		K_{R_3}=0.05	—	—	—	—	—	
H_2O		K_{RR}=0.616[k]	0.543	—	—	—	—	31
		$K_{RR'}$=−0.04	−0.0065	—	—	—	—	
		$K_{R\varphi}$=−0.022	0.0149	—	—	—	—	
		$K_{\varphi\varphi}$=0.055	0.0489	—	—	—	—	
H_2O		K_{RR}=0.496[k]	—	—	—	—	—	33
		$K_{RR'}$=−0.0064	—	—	—	—	—	
		$K_{R\varphi}$=0.024	—	—	—	—	—	
		$K_{\varphi\varphi}$=0.056	—	—	—	—	—	
H_2	analytical	0.6032[j]	—	—	—	—	—	37
		0.4085[k]	—	—	—	—	—	
LiH		0.0250[i]	0.0659	—	—	—	—	35
BeH		0.0796	0.145	—	—	—	—	
BH		0.207	0.195	—	—	—	—	
CH		0.319	0.281	—	—	—	—	
NH		0.455	0.387	—	—	—	—	
OH		0.554	0.498	—	—	—	—	
H_2O		K_{RR}=0.7269[j]	—	—	—	—	—	38
		$K_{RR'}$=−0.038	—	—	—	—	—	
		$K_{R\varphi}$=0.0183	—	—	—	—	—	
		$K_{\varphi\varphi}$=0.0593	—	—	—	—	—	
NH_3		K_{RR}=0.579[k]	0.442	—	—	—	—	39
		$K_{RR'}$=−0.0135	0.0064	—	—	—	—	
		$K_{\varphi\varphi}$=0.0552	0.0411	—	—	—	—	
		$K_{\varphi\varphi'}$=−0.0019	−0.0039	—	—	—	—	
		$K_{R\varphi}$=0.0289	0.0084	—	—	—	—	
		$K_{R\varphi'}$=−0.0064	0.0295	—	—	—	—	
CH_4		K_{RR}=0.470	0.347	—	—	—	—	39
		$K_{RR'}$=−0.0141	0.0087	—	—	—	—	
		$K_{\varphi\varphi}-2K_{\varphi'\varphi}+K_{\varphi\varphi'}$=0.0263	0.0315	—	—	—	—	
		$K_{\varphi\varphi}-K_{\varphi\varphi'}$=0.0604	0.0295	—	—	—	—	
		$K_{R\varphi}-K_{R\varphi'}$=0.0135	0.0096	—	—	—	—	

Table 1 (cont'd).

Molecule	Method of calculation of f.c.	Force constants (f.c.), a.u. quadratic theor.	quadratic expt *	cubic theor.	cubic expt	quartic theor.	quartic expt	Refs.
H_2	analytical	0.3241[a] 0.2487[c]	—	—	—	—	—	40
		0.0590[a] 0.0474[e]	—	—	—	—	—	40 29
Li_2		0.0154[l]	—	—	—	—	—	
Na_2		0.0103	0.0109	—	—	—	—	41
K_2		0.0051	0.0064	—	—	—	—	
NaH		0.0437	0.0507	—	—	—	—	
KH		0.0263	0.0360	—	—	—	—	
LiH		0.0730	—	—	—	—	—	
H_2		0.361[m]	—	−1.193	−1.264	—	—	
Li_2		0.0135	—	−0.0144	−0.0186	—	—	41, 42
Na_2		0.0097	—	−0.0085	−0.0107	—	—	
F_2		0.499	—	−1.287	−1.299	—	—	
H_2^+	I	0.0940[n]	—	—	—	—	—	
	II	0.0414	—	—	—	—	—	
H_2	I	0.343[o]	—	—	—	—	—	43, 44
	II	0.863	—	—	—	—	—	
H_2	I	0.549[p]	—	—	—	—	—	
	II	0.554	—	—	—	—	—	
H_2	I	0.434[q]	—	—	—	—	—	
	II	0.689	—	—	—	—	—	
H_2	I	0.294[r]	0.368	—	—	—	—	45
	II	−0.095	—	—	—	—	—	
H_2	I	0.293[s]	—	—	—	—	—	
	II	−0.065	—	—	—	—	—	
H_2	I	0.391[t]	—	−1.30	−1.258	—	—	
	II	0.337	—	−1.6	—	—	—	45
H_2	I	0.450[u]	—	−1.30	—	—	—	
	II	0.400	—	−1.37	—	—	—	
H_2	I	0.374[v]	—	−1.40	—	—	—	
	II	0.336	—	−1.15	—	—	—	
H_2		0.217[w]	—	−1.21	—	—	—	46
		0.265	—	−0.92	—	—	—	
		0.290	—	−1.02	—	—	—	
H_2I		0.356[m]	—	−1.294	—	—	—	47
Li_2I		0.0122	0.0141	−0.0150	−0.0188	—	—	
LiH		0.0726[a]	0.0659	−0.107	−0.116	0.154	0.154	
BH		0.219	0.195	−0.489	−0.501	0.990	0.997	
CH		0.198	0.281	−0.542	−0.860	1.287	2.056	23,48,49
NH		0.233	0.387	−0.789	−1.334	2.043	3.570	
OH		0.268	0.499	−1.068	−1.817	2.929	5.121	

Remarks: [a]The Hartree–Fock–Roothaan function calculated in terms of the one-determinant approximation. [b]Configuration interaction taken into account. [c]Two configurations only (TCO). [d]Optimised valence configuration (OVC). [e]Configuration interaction taken into account to a limited extent. [f]Extended basis set compared with c^7. [g]Basis set extended still further (compared with c^{11}). [h]One-determinant non-scaled wave function. [i]One-determinant scaled function. [j]One-determinant one-centre function. [k]One-centre function including configuration interaction. [l]Calculated from Eqn. (12). [m]Simple wave function of the molecular orbital type. [n]Wave function ($1S_a + 1S_b$) calculated on the basis of the virial theorem (I) and the Hellmann–Feynman theorem (II). [o]Wang function. [p]Coulson function. [q]Weinbaum function. [r]Non-scaled Heitler–London wave function. [s]Ditto for the molecular orbital wave function. [t]Scaled Wang wave function; [u]Coulson function; [v]Weinbaum function; [w]On the basis of a variational-perturbation scheme; [z]the anharmonic force constants for certain molecules were calculated by the authors of the review (they are not quoted in the relevant papers) in those cases where the original authors give an insufficiently complete set of spectroscopic constants.

*The experimental values were taken from the references given in column 9.

(experiment gives $K\alpha\beta = 0.3680$ a.u., $R_e = 1.401$ a.u., and $\omega_e = 4440\,cm^{-1}$). The results of this investigation and also the present authors' calculations[23] confirm the conclusion that, when the approximate Hartree–Fock function is close to the true Hartree–Fock function, one may expect a second-order perturbation error in the expectation value of the one-electron operator[24,25].

When account is taken of configuration interaction within the framework of the self-consistent field method, which leads to a correct dissociation limit, the force constants are improved provided that molecular orbitals with higher angular quantum numbers compared with the ground molecular orbital are included in the additional configurations.

Limited allowance for configuration interaction does in fact lead to a correct dissociation limit, but the force constants are not always improved. For example the inclusion by Fraga and Ransil[7] of additional configurations with the ground configuration resulted in a considerable improvement of the quadratic force constants of molecules such as HF and F_2, for which π configurations were included in the calculation (the error in the case of the one-determinant approximation is 49% for HF and 205% for F_2); however, poorer values of $K\alpha\beta$ were obtained for H_2, LiH, and Li_2, since molecular orbitals with higher angular quantum numbers than the ground molecular orbital were not included in the additional configurations of the molecules. This was also shown by Moser, Nesbet, and others[26-28] in Hartree–Fock calculations of the spectroscopic constants of the molecules H_2, CO, LiF, Li_2, and F_2, among which the last merits a more detailed consideration. In their study the wave function with configuration interaction, which is of the form

$$\Psi = \sum_k d_k \Phi_k ,$$

contains several optimised configurations obtained by replacing one of the σ orbitals of the ground configuration by orbitals of a different type. The method is based on a model according to which, when a molecule is formed from Hartree–Fock atoms or ions initially at infinite separation, changes occur mainly in the valence orbitals. This factor is taken into account by the introduction of optimised valence configurations (OVC), which are constructed by the promotion of the valence electron pair from the ground state to an allowed "excited" orbital. By minimising the total energy and the energy of the optimised valence configurations, equations defining the best values of d_k and the orbital coefficients were obtained. The calculations were made for the molecules H_2, Li_2, and F_2, only two configurations being optimised in the last case. We may note that in all cases the molecules dissociate into two Hartree–Fock atoms (Figs. 1 and 2). Dunham analysis gives, particularly for the optimised valence configurations in the case of the H_2 and Li_2 molecules, fairly satisfactory values of $K\alpha\beta$ (Table 1). Evidently this method is very promising for the calculation of spectroscopic constants by the numerical analysis of the potential curve, since it is based on a thoroughly developed expansion technique whilst retaining the simplicity and clarity of the shell model [moreover, the restriction to valence-excited configurations makes it possible to extend the method to systems with a larger number of atoms and to obtain a potential curve approximately congruent with the experimental curve for $R > R_e$ (Figs. 1 and 2), which shows that the correlation effects are partially taken into account]. Somewhat poorer results were obtained for F_2, compared with the other molecules, because the orbitals of the skeleton include orbitals such as $1\pi_u$ and $1\pi_g$, which are known to be of the valence type.

Among the earlier studies dealing with the LCAO-SCF method, with a limited allowance for configuration interaction, mention should be made of the work of Karo and Olson[29] (LiH) and Higuchi[30] (CH), the results of which also confirm the conclusion that molecular orbitals with higher quantum numbers than the ground orbital must be included in the additional configurations, and also the work of Boys et al.[31], where the force constants of the molecules BH and H_2O and the transition complex H_3 (the force constants of H_3 are not observed physically but are necessary for the prediction of reaction rates) were determined by the LCAO-SCF method with allowance for configuration interaction.

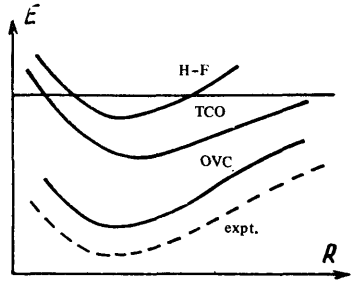

Figure 1.

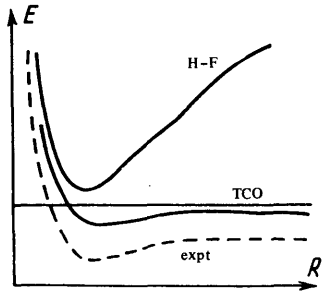

Figure 2.

Table 1 lists the force constant of the BH molecule obtained on the basis of a wave function, representing a linear combination of 23 Slater determinants and calculated for three internuclear distances, and the harmonic force constants of the H_2O molecule (in terms of the valence force system of coordinates[3]), the wave function of which was represented by a linear combination of 96 Slater determinants and calculated for seven nuclear configurations. The results are fully satisfactory for the diagonal force constants. The inconsistency of the results for the non-diagonal constants of H_2O both in magnitude and in sign can be accounted for largely by the errors in the derivation of the interpolation polynomial for the points at which the energy of the corresponding nuclear configuration was calculated.

The improvement of the Hartree–Fock calculations of the force constants by the introduction of configuration interaction has also been demonstrated in a recent investigation by Nesbet[32] of the electronic structure of C_2, which is the first of a series dealing with the study of the potential curves for the ground and certain excited states of the isoelectronic molecules C_2, BN, BeO, LiF, HeNe, and HNa. Here configuration interaction is introduced in two different ways: (1) two possible states which may be formed from four valence orbitals are considered and (2) two different orbital basis sets with six valence molecular orbitals are employed. Analysis of the potential curves shows a quantitative agreement between the experimental and calculated force constants. It is interesting that the statistical relations discovered by comparing the values obtained with experiment permit the prediction of the force constants of hitherto unobserved bound states, which are of interest, for example, for elucidating how molecules in an excited electronic state interact.

In concluding this review of numerical methods for the calculation of force constants, mention should be made of a number of studies[33–39] in which an interpolation procedure was also used to calculate the $K_{\alpha\beta}$, mainly for polyatomic molecules, but where the energies of various nuclear configurations were calculated using the one-centre approximation[36], which constitutes a variety of LCAO. A characteristic feature of the method is the employment of a basis set of functions centred on the same point, which makes it possible to avoid the calculation of many-centre integrals.

It should be noted that for hydrides of the type AH and AH_n the one-centre model both in the one-determinant approximation and with allowance for configuration interaction is very useful for the calculation of the quadratic force constants (Table 1). The one-centre approximation will be considered in greater detail below (p. 200 and p. 201) for reasons which will become clear later.

Summarising, it must be emphasised that the semiempirical methods developed at present for the numerical calculations of molecular force constants are extremely laborious and are applied mainly to diatomic molecules; moreover, the spectroscopic constants obtained by such calculations are still much inferior in their accuracy to the experimental constants, but the trend towards a reduction of errors in the calculations is quite definite.

III. ANALYTICAL METHODS FOR THE CALCULATION OF FORCE CONSTANTS

The analytical methods for the determination of force constants include the following: (1) analytical differentiation of the expression for the energy of the system obtained by a quantum-mechanical method; (2) the use of the differential Hellmann–Feynman theorem; (3) the use of the quantum-mechanical virial theorem; (4) the application of perturbation theory and various semiempirical variation-perturbation schemes.

Calculations of the harmonic force constants for a number of diatomic and polyatomic molecules based on the first procedure were made largely by Bratož and coworkers and also by Bishop and coworkers using both one-centre functions and Hartree–Fock–Roothaan functions in the self-consistent field approximation.

Thus the force constants of the molecules H_2 and LiH were calculated[40,50] from theoretical expressions obtained by Bratož[51] for the first and second derivatives of the total energy with respect to a parameter in terms of the LCAO-MO-SCF approximation and taking into account the configuration interaction[29]. It has been found that, when the method under consideration is employed, the molecular force constants agree better with experiment in the Fock–Roothaan one-determinant approximation than when limited allowance is made for configuration interaction, although the latter does in fact lead to a correct dissociation limit but not always to the best values of the force constants (Fig. 3). In other words, we encounter here an example illustrating the known fact that[25] an approximate wave function giving the best value of the operator for one physical quantity is not necessarily satisfactory for the calculation of the expected value of the operator for another physical quantity. In our case this means that the usual quantum-chemical variational solutions are more sensitive to the position of the limit (the value of the energy) than to the form of the potential surface (the force constants).

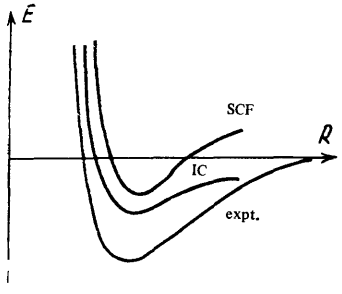

Figure 3.

Later it was shown[40] that, when the energy of the molecule is subdivided into the component E_n due to the interaction between the nuclei and the electrons of the skeleton and E_V due to the contributions of the electrons in the valence orbitals (such subdivision is always possible both in the self-consistent field method and in the method allowing for configuration interaction when in the latter case no account is taken of the excitation of the electrons of the skeleton), i.e.

$$E = E_n + E_v , \tag{10}$$

double differentiation yields

$$K_{\alpha\beta} = K_n + K_v . \tag{11}$$

It is found that $K_n \gg K_V$ for the force constants in the majority of diatomic molecules with a single bond (Table 1) and also for the diagonal force constants of molecules such as H_2O (Tables 2 and 3) and CH_4; this condition makes it possible to write

$$K_{\alpha\beta} \simeq K_n \simeq \frac{2}{R^3} . \tag{12}$$

Thus the main contribution to the force constants of the molecules considered is due to the interaction between the nuclei and the electrons of the skeleton. If the bond is not of a two-electron type, the results are less simple and Eqn. (12) no longer holds.

Bratož and coworkers arrived at a similar conclusion in their investigation [52,53] based on the one-centre model both in the one-determinant approximation and with allowance for configuration interaction, which is fairly acceptable, particularly within the framework of the analytical method for the differentiation of the energy of the system. Functions of this type describe satisfactorily the structure of hydrides the electrons of which are concentrated largely on one of the atoms and permit analytical differentiation of the matrix elements without additional limitations. It should be noted that, in contrast to such functions, the LCAO-MO-SCF functions require in their analytical evaluation on the basis of force constants the calculation of derivatives of many-centre integrals and also derivatives of orbital coefficients with respect to parameters. In view of the considerable difficulities in the solution of these problems, such calculations of the force constants are made largely on the basis of the simple wave functions of the molecular orbital and valence bond types (see below) and also the one-centre functions indicated above.

Table 2. The force constants of the water molecule (10^5 dyn cm^{-1}).

Force constant	K_n	K_v	$K_{\alpha\beta}$	Boys' data	Expt. (Ref.38)
$K_{\varphi\varphi}$	0.88	−0.01	0.87	0.86	0.77
$K_{R\varphi}$	0.31	0.05	0.36	−0.36	0.25
$K_{RR'}$	1.04	−1.11	−0.07	−0.62	−0.11

Thus, in terms of the one-centre approximation, it is easy to obtain [51,52] general formulae for the first, second, etc. derivatives of the energy of the ith state with respect to the nuclear coordinates, for example:

$$E_i^{x} = \sum_{s,t} d_{is}\, d_{it}\, H_{st}^{x} - \sum_{\alpha>\beta} Z_\alpha Z_\beta \frac{R_{\alpha\beta}^{x}}{R_{\alpha\beta}^{2}}, \qquad (13)$$

$$E_i^{xy} = \sum_{s,t} d_{is}\, d_{it}\, H_{st}^{xy} + \sum_{k}{}' [2/(E_i - E_k)] \times$$

$$\times \left(\sum_{s,t} d_{is}\, d_{kt}\, H_{st}^{x}\right)\left(\sum_{s,t} d_{is}\, d_{kt}\, H_{st}^{y}\right) + \sum_{\alpha>\beta} Z_\alpha Z_\beta (2R_{\alpha\beta}^{x} R_{\alpha\beta}^{y} - R_{\alpha\beta} R_{\alpha\beta}^{xy})/R_{\alpha\beta}^{3}, \qquad (14)$$

where d_{is} are the coefficients of the expansion in the wave function with configuration interaction in terms of the wave functions Φ_s of the united atom; H_{st}^{x}, H_{st}^{y}, and H_{st}^{xy} are the first and second derivatives with respect to the nuclear coordinates of the matrix element $H_{st} = \langle \Phi_s, H\Phi_t \rangle$. We may note that in the derivation of Eqns. (13) and (14) no approximation was made, since they are the true derivatives of the total energy for the given wave function with configuration interaction. The formulae will be particularly simple if it is postulated that the non-diagonal matrix elements are of the order of λ relative to the diagonal terms.

The calculation of the harmonic force constants with the aid of the one-determinant wave functions of the ground state, which is centrally-symmetrical, neglecting the second-order term [the first term is retained in Eqn. (14)], corresponds to Platt's electrostatic approximation‡, [54] i.e. to the hypothesis of a rigid electronic skeleton.

The application of the second order theory, i.e. the theory taking into account the second term in Eqn. (14), to calculations on polyatomic hydrides permits a detailed analysis of the various factors influencing the harmonic force constants of the molecules. This was done in the work of Bratož, Daudel, and others [52,53] for the H_2O and NH_3 molecules, the results of the calculations being compared, for water molecules, with the results of Boys [31], and also with experiment (Table 2).

Table 3. Force constants of the ammonia molecule (10^5 dyn cm^{-1}).

Force constant	1	2	3	$K_{\alpha\beta}$	Expt. (Ref.56)
K_{RR}	0.49	1.33	−1.79	9.03	1.17
$K_{RR'}$	0.88	0	−1.09	−0.21	0.08
$K_{\varphi\varphi}$	0.72	0.58	−0.44	0.86	0.91
$K_{R\varphi}$	0.26	0.36	−0.17	0.45	0.44
$K_{R\varphi}$	0	−0.36	0.26	−0.10	0.29
$K_{\varphi\varphi}$	0	−0.20	0.17	−0.03	−0.09

The fact that nuclear terms again make the main contribution to K_{RR} and $K_{\varphi\varphi}$ (as shown in Table 2) was demonstrated also in earlier studies by Longuet-Higgins and Brown [55] where the Platt model was applied to the polyatomic hydrides MH_n for the calculation of the stretching vibration frequencies on the basis of the electrostatic theorem.

Table 3, which gives the results of the calculation of various types of contributions to the harmonic force constants of the ammonia molecule, is also of interest. The first column corresponds to Platt's electrostatic approximation, which also makes the main contribution to the force constants K_{RR} and $K_{\varphi\varphi}$. When the wave function with configuration interaction, is employed, the contribution due to the introduction of additional configurations, neglecting the second term in Eqn. (14), is given in the second column; the electronic skeleton remains rigid as before ($d_{is}^{x} = 0$)—this is the so called "deformation" contribution. Finally, the third column lists the contributions due to the change in the wave function during vibrations, which is taken into account by the second term in Eqn. (14)—the "relaxation" contribution. The relaxation-deformation contributions play an appreciable role in non-diagonal force constants, particularly in $K_{R\varphi'}$ and $K_{\varphi\varphi'}$.

Thus the theory developed by Bratož and coworkers does not postulate that the wave function is spherical and that the electronic distribution is rigid [a rigid distribution is partly attained by taking into account the variation of the

‡We may note that Platt's model, which is based on two hypotheses (that the interatomic distance is close to $R_{1.0}$, the radius of the united atom in which the effective charge is unity, and that the force constant is approximately $4\pi\rho_{1.0}$, where $\rho_{1.0}$ is the electron density for the united atom at radius $R_{1.0}$), gives a satisfactory representation and prediction of the harmonic force constants for hydrides of the type AH.

linear coefficients d_{is} in the wave functions with the nuclear coordinates, which is in fact the reason for the appearance of the second term in Eqn. (14)].

It should be noted that Bishop and coworkers [33-35,37,39,57] carried out one-centre calculations of the force constants of a number of di- and poly-atomic hydrides (LiH, BeH, CH, BH, NH, OH, NH_3, H_2O, CH_4, and others), in different versions, corresponding to the removal of one or other limitation.

In a recent study by Bishop and Randic [38] the variation of non-linear parameters (orbital exponents) with the nuclear coordinates was included analytically in the expressions for the (harmonic) force constants of the H_2O molecule within the framework of the one-centre one-determinant wave function quoted by Allavena and Bratož. [33] The values of the force constants obtained here agree better with experiment than those calculated with the same accuracy but without taking into account the above relation (the agreement is better not only in magnitude but also in sign). In the same study the possibility of applying the authors' approach to one-centre functions, including configuration interaction, is also discussed.

Summarising, we may note that there is no doubt about the usefulness of further study of the functions under discussion, particularly for the calculation of anharmonic molecular force constants.

We shall consider further the possibilities of the differential Hellmann–Feynman theorem [58-60] and the quantum-mechanical virial theorem [61,62], which has recently found some application in the consideration of molecular forces [63-65] and force constants, mainly for diatomic molecules. The respective expressions for the theorems can be written as follows:

$$\frac{\partial E}{\partial x_\alpha} = \langle \Psi, \partial H/\partial x_\alpha \Psi \rangle, \tag{15}$$

$$\langle \Psi, T\Psi \rangle + E + \sum_{\alpha=1}^{N} X_\alpha \frac{\partial E}{\partial X_\alpha} = 0, \tag{16}$$

where, as usual, Ψ is the wave function for the system of $X_\alpha - 3N$ Cartesian coordinates (x_α, y_α, z_α) of N nuclei. It is seen from Eqns. (15) and (16) that the theorems yield the first derivative of the energy as the usual, expectation value of the corresponding operator, which permits $n - 1$ differentiations in order to obtain the nth derivative of the energy. As shown for the first time by Brown [66], the expressions for the harmonic force constants obtained by the differentiation of the Hellmann–Feynman theorem contain the integral of the derivative of the square of the modulus of the electronic wave function of the ground state with respect to a parameter (the internuclear distance in diatomic molecules).

Differentiation of the virial theorem for a diatomic molecule gives

$$K_{\alpha\beta} = \frac{1}{R_e}\left(\frac{\partial}{\partial R}\langle \Psi, V\Psi \rangle\right)_e, \tag{17}$$

or

$$K_{\alpha\beta} = -\frac{1}{R_e}\left(\frac{\partial}{\partial R}\langle \Psi, T\Psi \rangle\right)_e \tag{18}$$

Clinton [67] also concluded that the change in electron density cannot be ignored, since it is responsible for a non-vanishing contribution to the force constant. From this standpoint, he considered Platt's model, which remains attractive from the computational point of view, at least for diatomic hydrides, but is nevertheless purely formal.

Differentiation of the Hellmann–Feynman theorem makes it possible to express the force constant in the form [41]

$$K_{\alpha\beta} = Z_\alpha\left[Q_\alpha + \tfrac{4}{3}\pi\rho(\alpha) - \int \frac{\partial\rho}{\partial x_\alpha}\frac{\cos\theta_\alpha}{r_\alpha^2}d\tau\right]_e, \tag{19}$$

where Q_α is the electron density gradient at the nucleus α due to all the charges outside the limit of the nuclear radius (this term enters into the nuclear quadrupole coupling constant and may be obtained experimentally from the hyperfine structure of the rotational spectra [68] and $\rho(\alpha)$ is the charge density at the nucleus α. With regard to the last term in Eqn. (19), it can be shown, using either Eqn. (20), [96]

$$\frac{\partial\Psi}{\partial x_\alpha} = -\sum_n{}' \frac{(\partial H/\partial x_\alpha)_{0n}}{E_n - E_0}\cdot\Psi_n, \tag{20}$$

or the quantum-mechanical sum rule [42], that

$$-Z_\alpha\int\frac{\partial\rho}{\partial x_\alpha}\cdot\frac{\cos\theta_\alpha}{r_\alpha^2}d\tau = -2\sum_n{}'\frac{|(\partial V/\partial x_\alpha)|_{0n}^2}{E_n - E_0}, \tag{21}$$

the physical significance of which will be elucidated below. We may note that Eqn. (19) makes it possible to establish a relation between the force constant and the nuclear quadrupole coupling constant in a diatomic molecule, which is of considerable interest for theoretical chemistry.

Using the Hellmann–Feynman theorem, Salem [42] obtained second- and third-order force constants for the molecules H_2, Li_2, Na_2, and F_2 and also the force constants and the quadrupole coupling constants for diatomic hydrides from simple wave functions of the molecular orbital and valence bond type; on the basis of the properties of the electron density of the hydrides, it was shown that, for ionic hydrides of the type M^+H^-, Eqn. (19) becomes particularly simple and the force constants of these molecules can be expressed directly in terms of the quadrupole coupling constant:

$$K_{\alpha\beta} \simeq Q_H \simeq \frac{2}{R^3}.$$

Further mathematical forms which the force constants for di- and poly-atomic molecules can assume were investigated by Phillipson [43,69], who showed that the form of the equations depends on whether the virial or the Hellmann–Feynman theorem is employed and also on the coordinate system used to describe the wave functions.

Phillipson also studied the problem of the so called "stable" [70] functions, i.e. the approximate wave functions satisfying theorem (15). In the expressions which he obtained for the force constant account is taken of the dependence on internuclear distance of the parameters entering into the wave function:

$$K_{\alpha\beta} = \frac{1}{R_e}\left[\sum_i\left(\frac{\partial\bar{V}}{\partial\lambda_i}\right)\frac{d\lambda_i}{dR} - \frac{\bar{V}}{R^2}\right]_e, \tag{22}$$

$$\bar{V} = \langle \Psi(\lambda), V\Psi(\lambda)\rangle.$$

$$K_{\alpha\beta} = \left[-\sum_i(\partial\bar{F}/\partial\lambda_i)\frac{d\lambda_i}{dR}\right]_e,$$

$$\bar{F} = -\left\langle \Psi(\lambda), \frac{\partial V}{\partial R}\Psi(\lambda)\right\rangle, \tag{23}$$

where the summation is carried out with respect to all the variational parameters λ_i entering into the function Ψ. We may note that Eqn. (22) was obtained by differentiating Eqn. (16) on the assumption that the variational principle is satisfied, i.e. $dE/d\lambda_i = 0$, and Eqn. (23) was derived from Eqn. (15) on the assumption that the variational principle, the virial theorem, and the Hellmann–Feynman theorem are satisfied for all R.

Using simple wave functions of the molecular orbital and valence bond type, the force constants for H_2^+ and H_2 molecules were subsequently calculated [44] on the basis of Eqns. (23). Best agreement with experiment is achieved when Eqn. (22) is used, since none of the functions investigated satisfy theorem (15). The calculation suggests that, in order to obtain force constants comparable with the experimental values, it is necessary to have functions which describe accurately the curvature of the potential curve near R_e and satisfy the condition of zero force at the equilibrium point.

In a study by the present authors [47] which preceded those of Phillipson [43,44,59], the quadratic and cubic force constants of the H_2 and Li_2 molecules were calculated using relations of type (23) together with an investigation of the possibility of using the atomic wave functions with an angular variation of the effective charge to construct molecular wave functions satisfying the Hellmann–Feynman theorem. It was also shown that, when the condition $F_{R_e} = 0$ is satisfied and a reasonable relation between the parameters (for example the orbital exponents in atomic orbitals) and the internuclear distance is introduced leading to the accurate curvature of the potential curve, satisfactory agreement with experiment is obtained for both the force constants and the binding energy (Table 1), although the latter, as already pointed out, is not necessarily a criterion of the derivation of satisfactory force constants.

Benston and Kirtman [45] continued the studies of the various forms which the second- and third-order force constants of diatomic molecules can assume depending on which coordinates are chosen for the description of electronic motion; they calculated the force constants of H_2 molecules on the basis of functions of the same type (molecular orbital and valence bond). One can say (Table 1) that the force constants may be calculated with adequate accuracy with the aid of both theorems provided that scaled functions, i.e. functions for which the orbital exponents in the atomic orbitals are optimised for all R, are employed.

In a study by the present authors [23,48,49], a new method was developed for the calculation of force constants. It was shown that in the Hartree–Fock–Roothaan self-consistent field approximation it is possible to take into account the variation of the Fock–Dirac density matrix with parameters which depend on the coordinates of the nuclei. However, numerical evaluation of the latter expressions for the nth order derivatives with respect to parameters is associated with a fairly large volume of calculations, mainly the need to calculate the derivatives of two-electron many-centred integrals. The use of the virial theorems (15) and (16) made it possible to represent the force constants in terms of derivatives of the matrix elements of one-electron operators and thus avoid the above difficulty. We shall now quote formulae for the second- and third-order derivatives obtained by direct differentiation of the virial theorem formulated in terms of the LCAO-SCF procedure for diatomic molecules (in terms of a system of electronic coordinates linked with the centre of gravity of the molecule):[23]

$$K_{\alpha\beta} = -\frac{2}{R_e} Sp\left[\rho\frac{\partial T}{\partial R} - \rho(aT + \tilde{Ta})\right]_e,$$

$$K_{\alpha\beta\gamma} = -\frac{3}{R_e}K_{\alpha\beta} - \frac{2}{R_e} Sp\left[\rho\frac{\partial P}{\partial R} - \rho(aP + \tilde{Pa})\right]_e,$$

where $P = \partial T/\partial R - (aT + \tilde{Ta})$, $\rho = C\tilde{C}$, $a = \mu S^{-1}$ and μ is a matrix with the elements $\mu pq = <\partial\chi p/\partial R, \chi q>$.

Specific calculations of the force constants (up to the fourth order inclusive) performed on the basis of one-determinant Hartree–Fock–Roothaan functions for a number of diatomic hydrides and the water molecule [23,71] suggest that the method developed is applicable to the calculation of the potential functions for small molecules.

It is necessary to emphasise the importance of the condition that the approximate wave function employed should satisfy the virial and Hellmann–Feynman theorems if acceptable force constants are to be obtained (Table 1). Moreover, if one ensures that the Hartree–Fock function with a limiting-basis set is close to the true Hartree–Fock function, one may expect a second-order perturbation error in the calculation of the expected value of the one-electron operator [72].

The possibility of deriving theoretical expressions for derivatives higher than second order for the energy of diatomic molecules on the basis of theorems (15) and (16) has been demonstrated recently by Schwendeman [73]. The expressions obtained make it possible to establish rigorous relations between the experimental spectroscopic constants and derivatives of the kinetic and potential energies and hence permit assessment of the suitability of the quantum-mechanical calculations of the latter based on a particular approximate function. The same investigator [53] has carried out such an analysis for carbon monoxide; it consists in the following steps: the values of the total kinetic and potential energies found by Hartree–Fock calculations [11] were used to obtain by a numerical method the derivatives of these quantities with respect to R. These values are compared with those calculated with the aid of the relations indicated above. Thus it is possible to investigate the suitability of particular approximate Hartree–Fock functions for the calculation of force constants on the basis of the virial theorem. In this work on the carbon monoxide molecule, the satisfactory agreement of the calculated derivatives of T, V, and E suggests that there is no doubt that Hartree–Fock functions can be used in thise case. We may also note that, when scaled wave functions are employed, it is possible to achieve a more flexible R-behaviour of the potential curve [45,74].

We shall consider further a method based on the expansion of the electronic Hamiltonian in terms of powers of the displacement of the nuclei from the equilibrium positions with subsequent application of perturbation theory. The method was proposed by Brown [66], and has been developed and employed in a number of studies by Salem, Murrell, Bader, and others [41,42,75,76].

With the aid of second-order perturbation theory, the following expression was obtained for the harmonic force constant in the ground state:

$$K_{\alpha\beta} = \left[\left(\frac{\partial^2 H}{\partial R^2}\right)_{00} - 2\sum_n{}' \frac{|(\partial H/\partial R)_{0n}|^2}{E_n - E_0}\right]_e, \qquad (24)$$

which allows a physical interpretation of the following type: the first term is the average value of the operator d^2H/dR^2 at equilibrium and the second negative term reflects the variation of the force constant with the change in charge distribution caused by a change in the configuration of the molecule.

We must emphasise that the principal disadvantage of this approach and, incidentally, of any other where it is necessary to employ expansion (20) is the need to take into account the wave functions and energies of excited states, which are generally speaking unknown and, moreover, it is necessary to estimate the contributions from continuous energy states.

To eliminate this disadvantage, Benston and Kirtman [46] proposed another procedure [20] for finding the derivatives of the approximate wave functions. According to perturbation theory, the second- and third-order force constants for a diatomic molecule are expressed in terms of Ψ_0 and Ψ_1 respectively and the unperturbed and first-order wave functions. In turn $d\Psi/dR$ corresponds to the function Ψ_1, i.e. the problem reduces to finding Ψ_1. This is done by the variational method (the first attempt was made by Mills [77] for the CH_4 molecule). The formulae expressing $K_{\alpha\beta}$ and $K_{\alpha\beta\gamma}$ in terms of Ψ_0 and Ψ_1, found from the variational principle, are of the form

$$K_{\alpha\beta} \simeq \langle \Psi_0, H_2\Psi_0\rangle + 2\langle \Psi_1^{opt}, (H_0 - E_0)\Psi_0\rangle,$$
$$K_{\alpha\beta\gamma} \simeq \langle \Psi_0, H_3\Psi_0\rangle + 6\langle \Psi_1^{opt}, (H_2 - E_2)\Psi_0\rangle + 6\langle \Psi_1^{opt}, (H_1 - E_1)\Psi_1^{opt}\rangle, \quad (25)$$

where

$$H_n = \left(\frac{\partial^n H}{\partial R^n}\right)_e;$$

the expressions for E_n and Ψ_n are analogous.

For the H_2 molecule discussed by Benston and Kirtman [46], Ψ_1 was approximated by a linear combination of derivatives of the covalent and ionic functions from which Ψ_0 was derived.

The coefficients in the expression for Ψ_1 are then determined from the condition for an energy minimum in the second approximation. The results of the calculations agree well with experiment; for example, the Weinbaum function gives $K_{\alpha\beta} = 0.362$ a.u. and $K_{\alpha\beta\gamma} = -1.43$ a.u., while the experimental values are $K_{\alpha\beta} = 0.368$ a.u. and $K_{\alpha\beta\gamma} = -1.30$ a.u.

In general the different forms of Eqn. (24) obtained depending on the coordinate system chosen for the wave function are not readily susceptible to a quantitative analysis but they may be useful (as well as the expressions obtained from the analytical methods discussed above) for the understanding of the nature of the intramolecular forces. For example, Bader [76] employed such expressions for a qualitative physical interpretation of non-diagonal bond-interaction force constants in the potential function for polyatomic molecules (linear and non-linear triatomic and also pyramidal and planar tetra-atomic molecules), in particular in order to predict their magnitude and sign. It was found that both the magnitude and the sign of such constants are determined largely by the second term in Eqn. (24). It has been shown [75] for diatomic molecules that the first term of Eqn. (24) is largely responsible for the variation of $K_{\alpha\beta}$ in a series of isoelectronic molecules and the second changes steadily from one group of elements with identical nuclei to another, which permits the prediction of the direction of change in the force constant and is fully consistent with the above physical interpretation of the terms of Eqn. (24). Attention should be drawn to the fact that unfortunately very few studies dealing with the solution of this problem have been published in the Soviet literature.

One of the first studies on the application of analytical methods is that of Kovner and Tsimring [78] dealing with the determination of the harmonic force constants of the methane molecule. The idea of the one-centre approximation found an interesting development in investigations carried out in Veselov's laboratory. Thus, using the LCAO-MO method on the basis of a two-centre basis set, Bulychev [79] obtained the force constant for the stretching of the C ≡ C bond in acetylene, in good agreement with experiment; we believe that the force constant for the stretching of the C–H bond calculated by Bulychev is in good qualitative agreement with experiment and evidently the agreement can be improved by extending the basis set.

Adamov and Bulychev [80] carried out an improved calculation of the total energy of the H_2 molecule on the basis of the Weinbaum function corresponding to the superposition of covalent and ionic states; their analysis [80] of the potential curve made it possible to obtain spectroscopic constants in satisfactory agreement with the available data.

In conclusion we wish to express the hope that in the near future the above gap will be filled and that the numerical and analytical methods described here will permit the determination of the relative and absolute values of the potential constants, which will undoubtedly prove useful for the understanding of the nature of the forces between atoms in the molecule and also for the solution of spectrochemical problems.

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The Structure of Aqueous Non-electrolyte Solutions (Comparative Analysis of the Thermodynamic Properties of Aqueous and Non-aqueous Binary Systems)

Yu.I.Naberukhin and V.A.Rogov

A comparison of the thermodynamic properties of a large number of aqueous and alcoholic binary systems has established that the following properties are characteristic only of aqueous solutions: (1) negative enthalpies and entropies of mixing at low non-electrolyte concentrations; (2) negative partial molar entropies and enthalpies of water at moderate concentrations. The first property is evidence of the stabilisation of the water structure when the vacancies are filled. The second implies that the solution has a microheterogeneous structure owing to the presence in it of ordered regions (globules). The problem of the nature of the globules and their cooperative properties is discussed.
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1. INTRODUCTION

Concepts have recently developed as to the nature of the changes in the structure of water under the influence of a non-electrolyte dissolved in it. They reduce to the assertion that, when the vacancies in the water skeleton are filled by a non-electrolyte, the water structure is stabilised. This view explains various effects arising when small amounts of non-electrolytes are dissolved in water: the decrease of the self-diffusion coefficient, compressibility, and ion hydration and the increase of viscosity[1-5]. The filling of the vacancies in the water structure also accounts for the minima in the partial molar volumes of the non-electrolytes[6] and the anomalous variation of the solubility of gases[7,8] and certain other sparingly soluble substances[9].

Despite the abundance of studies and available data, we believe it useful to attempt to approach the problem of stabilisation from a purely thermodynamic standpoint without invoking beforehand any specific models of the water structure. Although the thermodynamic properties of aqueous non-electrolyte solutions have been discussed by Morachevskii[10,11] and Franks[12,13], we believe that one can proceed somewhat further by comparative analysis of the properties of aqueous and alcoholic binary systems. Only such analysis will make it possible to isolate the properties characteristic of aqueous solutions and justify the necessity for hypotheses concerning the collective interactions in aqueous systems. Using the method of comparative analysis, we shall also discuss, apart from stabilisation, the characteristics of the behaviour of aqueous solutions in the microheterogeneous region

(moderate concentrations of the non-electrolyte). In view of the inadequate treatment of this problem in the literature, here we will go beyond the framework of the thermodynamic description and will put forward a molecular mechanism for the phenomenon.

Sufficient experimental data have now been published to make such comparative analysis possible. However, it should be noted that, in the interpretation of the results obtained, most workers employ excess thermodynamic functions (with the usual notation H^E, S^E, and G^E) and not the functions of mixing (H^M, S^M, and G^M). We believe that such an approach is useful only when the system deviates little from ideal behaviour. For the alcoholic and aqueous solutions discussed below, this is known not to be the case. Here it is simpler to interpret directly the functions of mixing. Moreover, these functions can be used to assess the tendency of the solutions to form separate phases. In the present study we will therefore employ exclusively the thermodynamic functions of mixing.

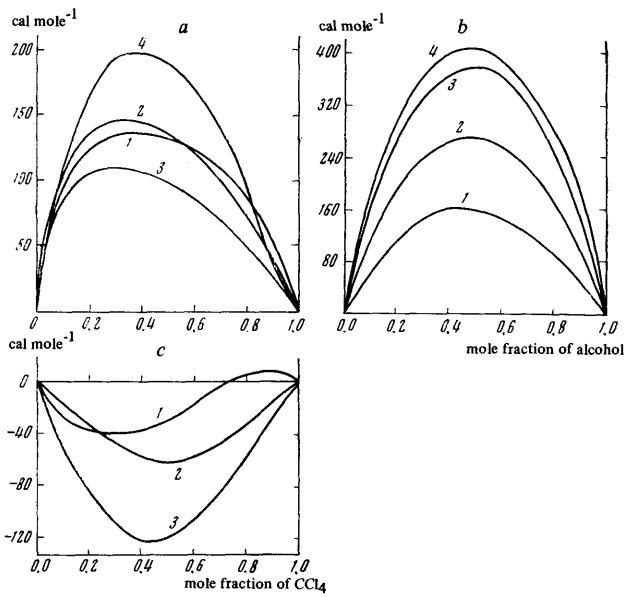

Figure 1. Enthalpy of mixing at 25°C for various systems: *a*) 1) ethyl alcohol–n-hexane; 2) n-propyl alcohol–n-hexane; 3) n-octyl alcohol–n-hexane; 4) isopropyl alcohol–n-hexane[14,15]; *b*): 1) methyl alcohol–acetone; 2) ethyl alcohol–acetone; 3) isopropyl alcohol–acetone; 4) s-butyl alcohol–ethyl methyl ketone[14,16]; *c*): 1) pyridine–carbon tetrachloride; 2) dioxan–carbon tetrachloride; 3) 3,5-dimethylpyridine–carbon tetrachloride[17,18].

2. LOW NON-ELECTROLYTE CONCENTRATIONS

The nature of the phenomena occurring in aqueous solutions at low (up to a mole fraction of 0.1) and moderate non-electrolyte concentrations is significantly different. Therefore in a comparative analysis of aqueous and alcoholic systems it is desirable to consider these two concentration ranges separately.

a. Enthalpy and Entropy of Mixing in Alcoholic Systems

At first sight it appears that the addition of any non-polar liquid to lower alcohols should lead to positive enthalpies of mixing H^M, since dilution of an associated liquid leads to the dissociation of some of the hydrogen bonds. This view is justified for systems of the alcohol–hydrocarbon type (Figs. 1*a* and 2) and also for systems of the alcohol–ketone type (Fig. 1*b*), although one cannot exclude *a priori* the possibility that hydrogen bonds are formed between alcohols and ketones. For this reason, the finding that the mixing of lower alcohols with carbon tetrachloride, a classical inert solvent, at fairly low temperatures leads to negative values of H^M, indicating a powerful interaction between the alcohol and carbon tetrachloride (Fig. 3), is all the more surprising. This increase of H^M cannot be accounted for by the interaction of carbon tetrachloride with the hydrocarbon "tail" of the alcohol, since, first, on passing to higher alcohols, H^M increases and becomes positive (Figs. 3*a* and 3*b*) and, secondly, H^M for the mixing of hydrocarbons with carbon tetrachloride is positive[23]. The increase due to the van der Waals interaction between carbon tetrachloride and the proton of the OH group is evidently also impossible, since the replacement of a strong hydrogen bond by a van der Waals interaction cannot lead to an energy gain.

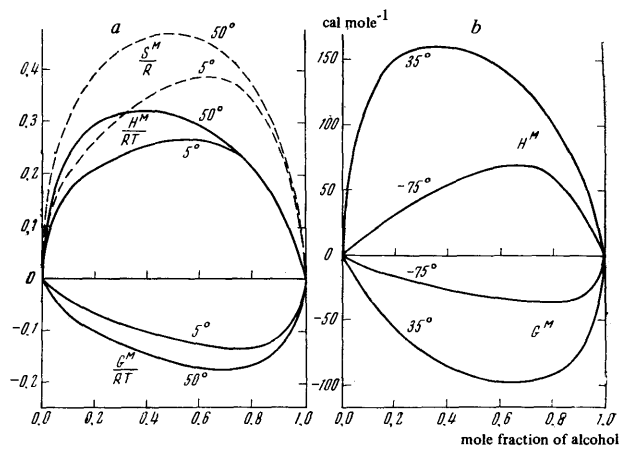

Figure 2. Thermodynamic functions of mixing for various systems:
a) ethyl alcohol–cyclohexane[19]; *b*) ethyl alcohol–methylcyclohexane[20].

Thus only one explanation remains: the increase of H^M at low carbon tetrachloride concentrations in alcohol is due to powerful van der Waals interactions between carbon tetrachloride molecules and the *p*-orbitals of the alcohol oxygen atoms not involved in hydrogen bonding. Each alcohol molecule has two possibilities of forming a hydrogen bond via oxygen and only one via hydrogen. Thus even in a completely self-associated alcohol each of its molecules retains on average one possibility of forming an additional hydrogen bond. Since hydrogen bonds in alcohols do not form a three-dimensional network but lead to

chain or ring structures[24-27], the carbon tetrachloride molecule can come into contact with the oxygen atom of the alcohol without affecting the hydrogen bond. The validity of this explanation is confirmed by the negative value of H^M in dioxan–carbon tetrachloride and pyridine–carbon tetrachloride systems (Fig. 1*c*). On the other hand, the large increase of H^M in the methanol–chloroform system (Fig. 4*a*), due to the formation of a hydrogen bond between chloroform and the alcohol, is evidence of the absence of steric hindrance to van der Waals interaction between carbon tetrachloride and the oxygen atom of the alcohol. Another system where an increase of H^M is observed below −50°C is ethanol–toluene (Fig. 5*a*). Probably this effect can also be accounted for by ready van der Waals interaction between the benzene ring and the oxygen atom.

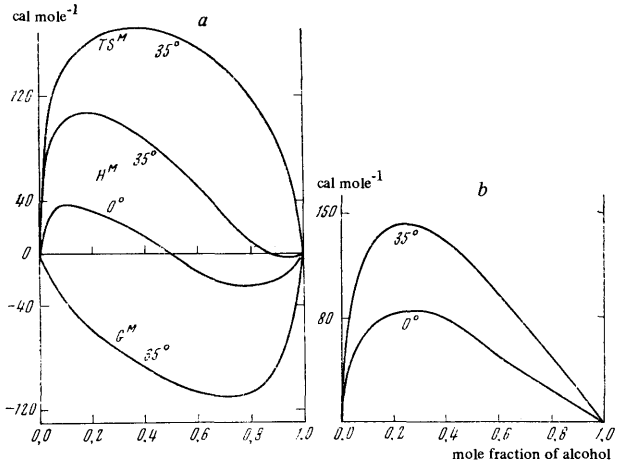

Figure 3. *a*) Thermodynamic functions of mixing for the methyl alcohol–carbon tetrachloride system[21,22]; *b*) enthalpy of mixing in the n-octyl alcohol–carbon tetrachloride system[22].

The above data allow the following conclusions to be drawn: the sign and magnitude of H^M in alcoholic systems can be various and are determined by the characteristics of the interaction of the alcohol with the second component in each specific case. In contrast to the enthalpy, the entropy of mixing in all the systems considered shows the same behaviour and is positive †.

b. Entropy and Enthalpy of Mixing in Aqueous Solutions

Fig. 5*b* and Figs. 6–11 present the heats of mixing for various binary aqueous systems. A characteristic feature of all these curves is the negative sign of H^M at low concentrations of the second component (and at sufficiently low temperatures). Moreover, the enthalpy of mixing is negative also for the dissolution in water of aliphatic and aromatic hydrocarbons and even the inert gases[35,36]. Thus one may assert that the dissolution in water of the majority of non-electrolytes takes place with evolution of heat. This behaviour is an important property of aqueous systems and sharply distinguishes them from the alcoholic solutions discussed above.

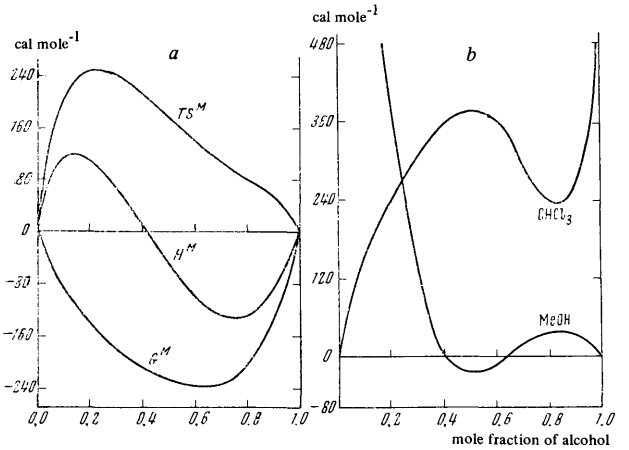

Figure 4. The methyl alcohol–chloroform system at 35°C: *a*) thermodynamic functions of mixing[21]; *b*) partial entropies $T\bar{S}_i^M$ of the components.

We shall now attempt to discover the reasons for such behaviour of H^M in the specific example of the water–acetone system. If the energy gain on mixing the two liquids is regarded as the result of only the pair interactions between their molecules, the negative value of H^M can be accounted for in two ways: (1) the formation of a hydrogen bond between acetone and water; (2) powerful van der Waals interaction between acetone and water.

However, the first hypothesis must be immediately rejected. Indeed, the formation of a hydrogen bond between acetone and water is possible only at the expense of the dissociation of the stronger water–water hydrogen bond; moreover, H^M for the mixing of acetone with alcohols is positive (Fig. 1*b*) and it would be difficult to understand why acetone associates with water but not with alcohols. This explanation is also unsatisfactory because it is not universal and is not applicable, for example, to the dissolution of hydrocarbons and noble gases in water.

The second explanation, based on a powerful van der Waals interaction, requires a more detailed examination. In the first place it is necessary to resolve the difficulty mentioned above: the different signs of H^M in the dissolution of acetone in alcohols and water. The overall heat of solution of acetone consists of the energy loss resulting from the interactions between the molecules of the solvent and the energy gain from the interactions between the solvent and acetone. However, the energy differences between the water–water and alcohol–alcohol interactions are not very great; the same may be said of the alcohol–acetone and water–acetone interactions. Therefore, in order to account for the negative sign of H^M in water, it is necessary to postulate that there is no large positive

† There is no need to quote S^M curves for all the systems in support of this assertion, since the entropy of mixing cannot be negative if $H^M > 0$ (by virtue of the relation $TS^M = H^M - G^M$ and $G^M < 0$). The positive sign of S^M for systems with $H^M < 0$ is illustrated in Figs. 3*a* and 4*a*.

contribution to H^M due to water–water dissociations. We arrive at a similar conclusion by considering other aqueous solutions. Consequently this phenomenon is not caused by the properties of the non-electrolyte but the characteristics of the water structure, i.e. it is necessary to assume that water contains fairly large cavities (vacancies) which accommodate non-electrolyte molecules on dissolution.

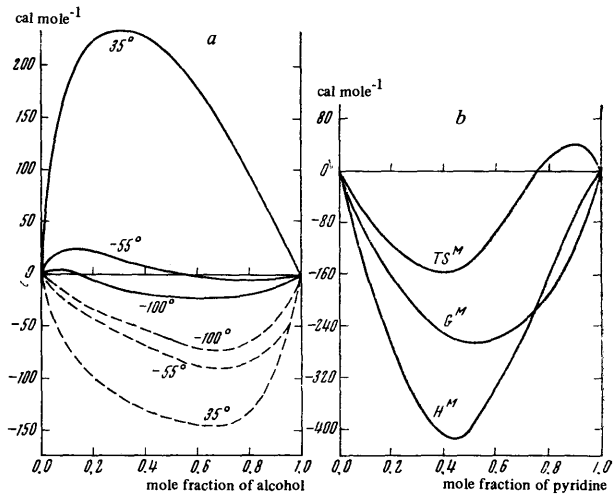

Figure 5. Thermodynamic functions of mixing for various systems:
a) ethyl alcohol–toluene[20] (continuous line—H^M; dashed line—G^M); *b*) water–pyridine at 20°C[28].

The existence of cavities, which is a distinctive feature of the structure of water, may be confirmed by considering the partial molar enthalpies of non-electrolytes on infinite dilution $\bar{H}^M_{H,O}$. In the majority of the systems examined (Figs. 5*b*, 6–9, and 11) $\bar{H}^M_{H,O}$ amounts to 1–3 kcal mole^{-1} in absolute magnitude. This exceeds by several hundred cal mole^{-1} not only the values of $\bar{H}^M_{i,O}$ observed in systems with powerful van der Waals interaction between the components [for example, carbon tetrachloride–dioxan, carbon tetrachloride–pyridine, and carbon tetrachloride–methanol (Figs. 1*c* and 3*a*)], but even the $H^M_{i,O}$ in certain systems with hydrogen bonds [for example, chloroform–dioxan[37], chloroform–acetone[38], and chloroform–methanol (Fig. 4*a*)]. Clearly such a large negative heat change could be accounted for by van der Waals interactions only if it is assumed that water–water bonds are not dissociated on mixing.

However, it is doubtful if these large heat changes are completely determined by van der Waals pair interactions. Indeed, comparison of the values of $\bar{H}^M_{H,O}$ on dissolution in water of alcohols, ketones, hydrocarbons, and the inert gases shows that the heat change is virtually independent of the polarity of the second component although a dependence would be expected for van der Waals interactions.

The inadequacy of the hypothesis of van der Waals interactions alone becomes evident when the entropy of mixing is considered. Comparison of Figs. 5*b* and 6–11 shows that S^M is as a rule negative for all aqueous systems at low concentrations of the second component and at low temperatures, while for all other liquids (see, for example, Fig. 1–4 and 5*a*) S^M is positive even if the mixing is exothermic. The negative sign of S^M is an important characteristic of aqueous solutions, which distinguishes them from other binary systems.

Nevertheless, when water and a non-electrolyte are mixed, a positive contribution to the entropy of the system appears, as for any other two liquids, owing to the interchange of molecules of water and of the second component. The van der Waals interaction between the components leads to a decrease of S^M compared with S^M_{id} but its sign still remains positive. These considerations are fully confirmed by experimental data: we are not aware of a single system without hydrogen bonds where a negative entropy of mixing is observed.

A negative contribution to entropy in the pair interaction between species can arise only if they form a complex, say via hydrogen bonding. However, we have already rejected this possibility for water–non-electrolyte systems. Therefore one must assume that the negative entropy of mixing in these systems is not caused by pair interaction between water and non-electrolyte molecules, but by collective changes in the water structure towards greater order. In such a process the enthalpy of the system should also fall ($\Delta H = \Delta G + T\Delta S < 0$) which makes a contribution to the heat change, additional to the van der Waals interactions. All these collective phenomena have come to be referred to as the stabilisation of the water structure. The energy gain on stabilisation implies that the dissolution in water of small amounts of non-electrolytes does not lead to the dissociation of some of the hydrogen bonds, as in all other highly self-associated liquids, but in fact results in the formation of a certain number of water–water hydrogen bonds or in their strengthening ‡.

Although the conclusion that the concept of stabilisation must be introduced is not based on any particular model of the water structure, it is useful to illustrate the significance of this term with reference to a specific model, for example that of Samoilov[39,40], according to which water consists of molecules forming an ice-like framework blurred by thermal motion and of molecules partially filling the vacancies in the framework. When a non-electrolyte is added to water, it enters the cavities within the framework (without dissociating the hydrogen bonds or disrupting the van der Waals water–water interactions) and displaces some of the "cavity" water molecules to the framework, since by filling part of the cavities it displaces the dynamic equilibrium between the "cavity" and "framework" water molecules[41]. Since this involves the formation of new water–water hydrogen bonds, the enthalpy of mixing should be negative. On the other hand, the transfer of some water molecules to the more ordered phase (the framework) leads to a negative entropy of mixing.

The water–pyridine system requires special consideration. Although here too negative values of S^M are observed (Fig. 5*b*), they cover an unduly wide concentration range. One cannot postulate that the effect associated

‡ The effects associated with stabilisation should evidently decrease with temperature owing to the breakdown of the water structure. This is in fact observed (Figs. 7 and 9).

with stabilisation can be observed up to a pyridine concentration of 50 mole %, where the water structure is certainly disrupted. Probably the explanation of the negative values of S^M for this system consists in the fact that pyridine forms very strong hydrogen bonds with water. Indeed, H^M for this system is high and negative over the entire pyridine concentration range. This explanation is also confirmed by vibrational spectra [42,43]. Probably the behaviour of thermodynamic functions in the water–dimethyl sulphoxide [44,45] and water–diethylformamide systems [46] should be explained similarly.

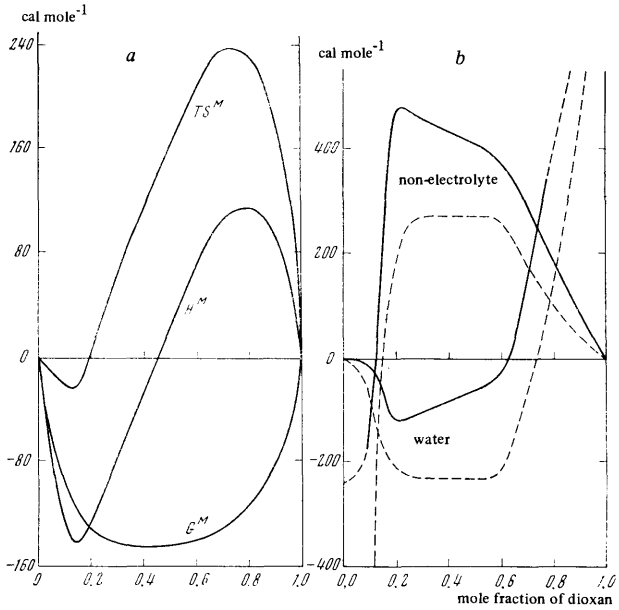

Figure 6. The water–dioxan system at 25°C; *a*) thermodynamic functions of mixing [29]; *b*) partial entropies $T\overline{S}_i^M$ (continuous line) and enthalpies $\overline{H}_i^M$ (dashed line) of the components.

The stabilising effect of the non-electrolyte entering the cavities in the water structure should be reduced with increase of the non-electrolyte concentration. This accounts for the characteristic S shape of the plots of S^M and H^M in aqueous systems against concentration: the negative contributions to S^M and H^M owing to stabilisation are replaced at high non-electrolyte concentrations by positive contributions from the dissociation of water–water hydrogen bonds. It would be extremely interesting to establish the concentration corresponding to maximum stabilisation or, what amounts to the same thing, to the optimum filling of the cavities. The minima in H^M, S^M, or the excess partial volume $\overline{V}_H^E$ are usually compared with this concentration. However, there is a difficulty here. If the stabilising effect of the non-electrolyte and the disruption of the structure are described by fairly smooth concentration functions, the extrema in H^M, S^M, and $\overline{V}_H^E$ need not coincide, since they are a consequence of the superposition of different functions varying in the opposite sense. Then the significance of the term "maximum stabilisation" becomes extremely indefinite. This situation in fact obtains. For example in the water–dioxan system at 25°C a minimum in the excess partial volume of dioxan is observed at a non-electrolyte mole fraction of 0.04, [47] while the minima in H^M and S^M occur at mole fractions of 0.13 and 0.12 respectively (Fig. 6*a*). The extrema in all the functions should coincide only when the stabilisation varies sharply with concentration, for example, when one can speak of the exact instant when the cavities are filled. However, in such a case it would be necessary to seek additional explanations of the observed differences in the positions of the extrema. This dilemma cannot be resolved solely on the basis of thermodynamic data. The first view appears more prudent. Having adopted it, one can assume that the stabilising effect of the non-electrolyte hardly extends beyond concentrations where its mole fraction is 0.10–0.15.

Summarising the above discussion, one may assert that (1) at low non-electrolyte concentrations aqueous solutions exhibit unique properties, which consist in the fact that, regardless of the nature of the second component, the entropy and enthalpy of mixing are negative and (2) these facts provide evidence of a collective stabilisation of the hydrogen bond lattice on addition of a non-electrolyte to water due to an increase in the energy of the hydrogen bonds or in their number.

3. MODERATE CONCENTRATIONS

We shall now consider the behaviour of the thermodynamic functions of mixing for non-electrolyte concentrations corresponding to a mole fraction of 0.2 and above, i.e. in the region where the water structure is disrupted. In the first place we must note that the G^M–concentration curve has sections with low curvature, which are particularly distinct in the water–dioxan system for dioxan mole fractions in the range 0.25–0.6 (Fig. 6*a*). These indicate that the system tends to form two layers, i.e. microheterogeneity of the structure of the solution. Such behaviour of G^M is not in itself an exclusive characteristic of aqueous mixtures, since sections with low curvature on G^M–x curves are encountered fairly frequently in binary systems with positive deviations from ideality (see, for example, Figs. 2, 3*a*, 4*a*, and 5*a*). The particular properties of aqueous solutions are shown in the unusual behaviour of the partial enthalpies and entropies of mixing in the region of microheterogeneity, namely (1) in all systems (with the exception of water–methanol mixtures) $\overline{H}^M_{water}$ and $\overline{S}^M_{water}$ are negative over a considerable concentration range at not unduly high temperatures (see Fig. 6*b*; similar behaviour follows from Figs. 5*b* and 6–11) and (2) in a series of aqueous systems there is a rigorously linear relation between H^M and concentration with corresponding horizontal sections in H_i^M–x curves (Figs. 6, 7*a*, and 9*b*)§.

The first characteristic is indeed an exclusive property of aqueous solutions. In all the non-aqueous systems examined, the partial molar entropies of mixing of both components always proved to be positive. We succeeded in finding only one system which is an exception to this rule, namely methanol–chloroform (Fig. 4*b*).

§ The linearity of the H^M–x relation has been established very reliably. Thus in the water–dioxan system 7 experimental points lie on a straight line [29] and in the system water–t-butyl alcohol 5 points [32].

Here, the negative values of $\bar{H}^{M}_{meth}$ and $\bar{S}^{M}_{meth}$ can evidently be explained by the formation of hydrogen bonds between methanol and chloroform, which can occur without the dissociation of alcohol–alcohol hydrogen bonds, i.e. the reason for the anomalous behaviour of the thermodynamic functions for this system consists in the unusual nature of the proton donor–acceptor properties of the alcohol, to which attention has already been drawn in the first section of the review. Thus the negative partial entropy of mixing is typical only for aqueous systems and therefore must be associated with the characteristics of the water structure.

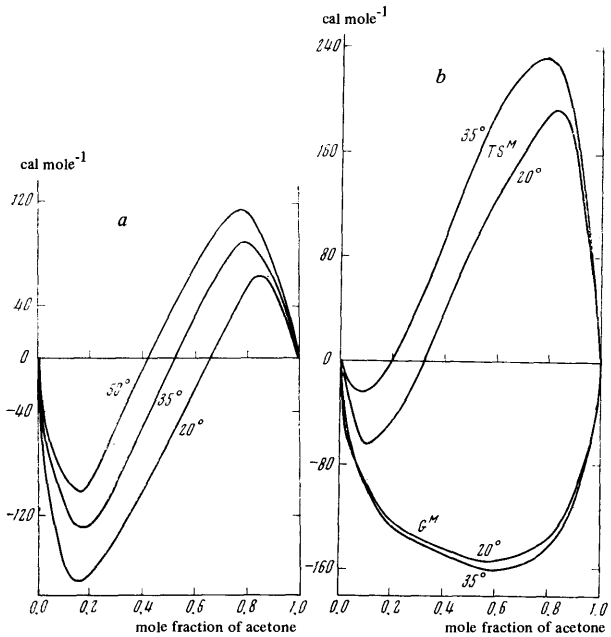

Figure 7. The water–acetone system: *a*) enthalpies of mixing[30]; *b*) entropies and free energies of mixing[31].

The retention of the negative sign of H^{M}_{water} and S^{M}_{water} over a wide range of concentrations, up to a non-electrolyte mole fraction of 0.7, is evidence of the existence in solution at these concentrations of regions where water molecules exhibit a fairly high degree of order. Indeed, by definition, the partial molar entropy of water is the entropy of mixing of a large volume of solution at a given concentration with one mole of water. If the solution is a homogeneous mixture of association complexes of water and the non-electrolyte, the degree of order in water should decrease when it is added to the solution, since water–non-electrolyte complexes are weaker than water–water complexes. Contrary to experiment, this leads to positive values of $\bar{H}^{M}_{water}$ and $\bar{S}^{M}_{water}$. Consequently we are obliged to attribute to this solution a microheterogeneous structure which contains regions (globules) where water exists in an even more ordered state than in pure water. When the added water enters these regions, negative values of $\bar{S}^{M}_{water}$ and $\bar{H}^{M}_{water}$ are in fact obtained. However, in a heterogeneous system of this kind there is another possible mechanism leading to the negative signs of $\bar{S}^{M}_{water}$ and $\bar{H}^{M}_{water}$: the added water can displace the equilibrium between the globules and the disordered phase towards the former. Therefore the assertion that globules are more ordered than pure water is not justified.

We must emphasise that the conclusion that ordered regions (globules) exist in aqueous solution is a fact. It follows logically from two factors: (1) the negative sign of $\bar{S}^{M}_{water}$ and $\bar{H}^{M}_{water}$ and (2) the assertion that water–non-electrolyte association complexes are less stable than the water–water complexes. The first is an experimental fact in the systems investigated; the validity of the second follows from the endothermic heat of solution of water in pure electrolytes (n-propyl alcohol, t-butyl alcohol, acetone, and dioxan) and has also been demonstrated spectroscopically for the case where the non-electrolyte is acetone or dioxan[42,43]. According to this reasoning, we are not justified in assuming that the globules are present in the water–pyridine system, where the second factor does not apply[42,43], and in alcohol–non-electrolyte systems, where the first factor does not hold.

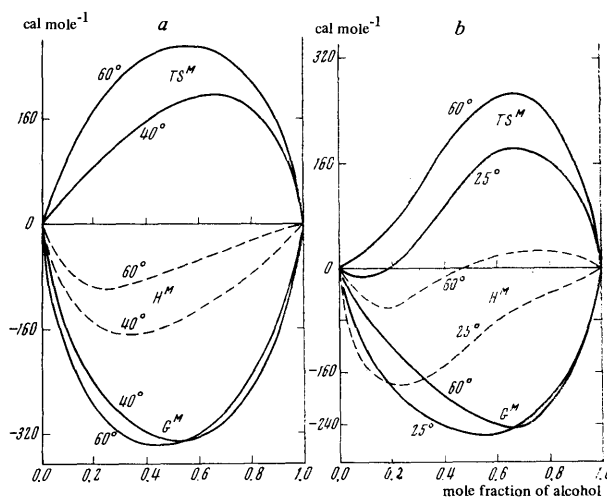

Figure 8. Thermodynamic functions of mixing for t-butyl alcohol systems[32].

We shall now examine the nature of the ordered globules in aqueous solutions. Here we cannot afford to remain at the factual level and must proceed to hypothetical considerations. The following situation is extremely probable. We have seen that a small amount of non-electrolyte leads to definite changes in the water structure, which entails a gain in stabilisation energy as a result of the collective interactions of water molecules. When the electrolyte begins to disrupt water–water hydrogen bonds after filling the cavities, a continuous disintegration of their three-dimensional lattice proves to be more difficult than the fragmentation of the water structure into fairly large structured regions in which collective stabilisation is still possible. In other words, at moderate concentrations the electrolyte can be more readily accommodated in the

interstices between the globules. Then a kind of separation into different phases takes place in the solution: into the "phase" of structured water which contains also a small amount of non-electrolyte (for example in the cavities within the structure) and a disordered "phase" consisting of non-electrolyte molecules and individual water molecules associated with them. We shall refer to such separation into microphases as microlayer formation.

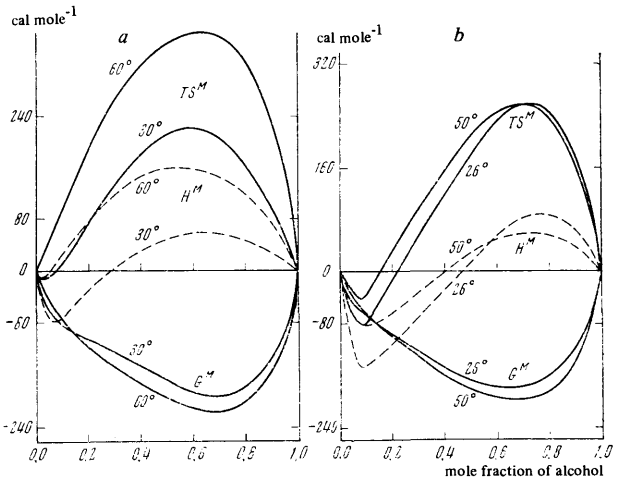

Figure 9. Thermodynamic functions of mixing for various systems:
a) n-propyl alcohol–water [10]; *b*) t-butyl alcohol–water [32].

It is important to emphasise yet again that the reason for the formation of globules is the energy gain due to the collective interactions of water molecules and made possible by the particular structure of the globules¶. The presence of stabilisation energy implies that the globules are thermodynamically stable species and cannot be regarded as fluctuations. Therefore the microlayer formation described here is a very special case of the tendency of solutions to form separate phases, which is usually understood as resulting from the development of concentrations fluctuations.

We shall now attempt to explain the significance of the second characteristic of the behaviour of the thermodynamic functions of mixing of aqueous systems in the region of microlayer formation. The constancy of the partial enthalpies can be most simply accounted for if it is assumed that the non-electrolyte (or water) added to the system always enters an identical molecular environment, which happens, for example, in true phase separation. In the case of microlayer formation, this condition will be fulfilled if the composition of the microphases (globules and disordered regions of the solution) remains constant in the concentration range considered. The composition of the microphases should then correspond to the boundary points of the linear section in the H^M plot. For example, in the water–dioxan system the microphases have the composition (in mole fractions) 0.25 dioxan + 0.75 water and 0.6 dioxan + 0.4 water.

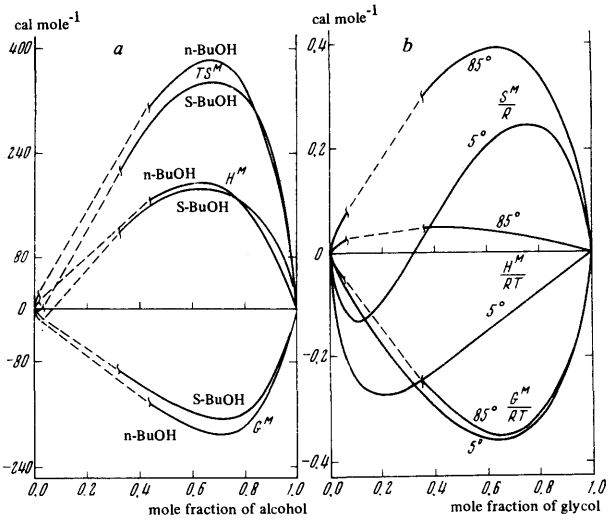

Figure 10. Thermodynamic functions of mixing for various systems:
a) n-butyl alcohol–water and s-butyl alcohol–water at 60°C [10] (dashed line—layer formation region); *b*) water–butane glycol [33].

However, the constancy of the composition of the microphases in microlayer formation is not yet sufficient to ensure the linearity of the variation of H^M. In addition, one must assume that, when the concentration of the solution changes, the dimensions of the globules remain constant and only their number changes. Indeed the enthalpy of the system considered consists of three terms: (1) the enthalpy of the molecules in the disordered phase; (2) the enthalpy of the molecules in the globules; (3) the enthalpy of the interaction of these two "phases". If it is assumed that the dimensions of the globules change, the last two terms will not vary linearly with concentration and special hypotheses are necessary to ensure the linearity of their sum. At the same time the constancy of the dimensions of the globules automatically entails the linearity of the $H^M - x$ relation. Such constancy does not appear strange if account is taken of the above hypothesis that the microphases have constant composition. It therefore follows that, when the concentration of the solution is altered, the molecular environment of the globule remains unchanged. Only the distances between the globules alter, and this should not affect their dimensions.

It is also possible to account for the constancy of the composition of the microphases. The constancy of the composition of the globule is associated with the limited number of the cavities in it. On the other hand, the constancy of the composition of the second "phase" is ensured by the fact that, when the concentration of water in it exceeds a certain critical value, a new globule separates.

¶ We shall not specify the mechanism of the collective interaction. Frank [48,49], who was the first to introduce the hypothesis of the globules (in pure water), believed that this involved the mutual polarisation of water molecules, leading to a strengthening of the hydrogen bonds.

This becomes understandable if we recall that the dimensions of the globules remain constant in the region of microlayer formation, i.e. the globule decomposition processes and hence the globule formation processes are cooperative.

The suggested hypothetical mechanism explains in a natural manner why microlayer formation is revealed more clearly by H^M than by G^M: the curvature in the plot of G^M arises from the entropy of mixing, which contains a non-linear contribution from the exchange of the microphases. This factor makes it possible to estimate roughly the number of molecules in the globule. It it is assumed that the dimensions of both microphases are equal, the maximum energy of their exchange is S_{id}/ν, where S_{id} is the maximum entropy of mixing of the ideal solution and ν is the number of molecules in the globule. This quantity must be set equal to the maximum deviation of the S^M-x relation (or, what amounts to the same thing, the $G^M/T-x$ relation) from linearity in the region of microlayer formation. For the three systems water–dioxan, water–acetone, and water–t-butyl alcohol, ν is approximately 40–80 molecules.

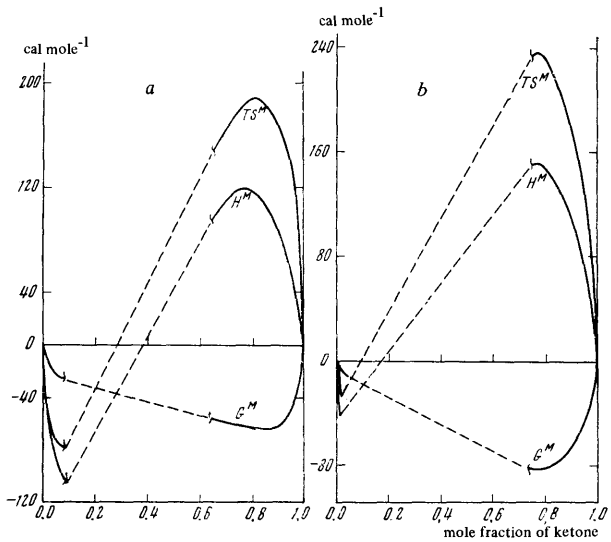

Figure 11. Thermodynamic functions of mixing for various systems:
a) water–ethyl methyl ketone at 20°C [34]; *b*) water–cyclohexanone at 20°C [34] (dashed line–layer formation region).

The experimental finding that the excess volume of the solution V^E is not a linear function of concentration in the region of microlayer formation [47] (in contrast to true phase separation) is also consistent with our microlayer formation model. The point is that the free volume in the packing of particles of different kinds makes a significant contribution to V^E. It is reasonable to suppose that the free volume in the packing of two different microphases in aqueous solution differs from the free volume in the packing of water and non-electrolyte molecules. This in fact leads to the non-linearity of the V^E-x relation.

Thus, at moderate concentrations aqueous solutions also show unusual properties, which must be attributed to the presence in the solution of regions with a high degree of order (globules). Globules probably arise from the mutual stabilisation of water molecules and probably possess (over a concentration range) cooperative properties.

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Correlation Equations in Free-radical Reactions

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This review deals with the methods of correlation analysis which have been applied to studies of the kinetics of free-radical reactions. It discusses the use of the Hammett and the Taft equation, of the Alfrey-Price scheme, of the Bamford equation, and also the correlations with quantum-mechanical parameters and various additive empirical methods. Polar and resonance effects in free-radical reactions are quantitatively separated by a two-parameter scheme based on the Taft equation. The relationship between the structure of the transition state and the reactivity of the free radicals is considered. 265 references.

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I. INTRODUCTION

The basic factors which determine the reactivity of free radicals towards compounds able to react with them (substrates) have already been identified. They include the polar, the resonance, and the steric effect, the dissociation energy of the bond, the type of hybridisation of the atom to which the unpaired electron is attached, etc. In general, these parameters are not mutually independent, and therefore the problems consist not so much in allowing for all the factors which may affect the reactivity of the free radical as in choosing the smallest number of such parameters which are mutually independent or approximately so.

Unfortunately, there is as yet no way of expressing the reactivity of a free radical in terms of even the three basic reaction effects (polar, resonance, and steric). Existing correlation equations apply to specific cases in which one or two of the basic effects are predominant. In the following Sections we shall discuss the correlation equations proposed by various authors for a quantitative description of the reactivity of radicals and substrates, and we shall attempt to apply the two-parameter correlation scheme to free-radical reactions.

II. CORRELATION WITH KINETIC AND THERMODYNAMIC PARAMETERS

1. The Hammett Equation

The Hammett equation - the most widely used correlation equation - was originally applied only to heterolytic reactions. This empirical relationship gives the ratio of the rate (or equilibrium) constants for the reactions of unsubstituted or substituted benzene derivatives in terms of constants[1] of the *para*- and *meta*-substituents (σ):

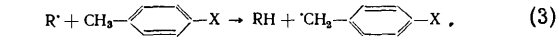
$$\lg \frac{k_{sub}}{k_0} = \rho\sigma \qquad (1)$$

where ρ is a proportionality constant. The values of σ were obtained by Hammett by comparing the dissociation constants of substituted benzoic acids. The σ constants are usually believed to characterise the polar effect of the substituent, transmitted through the σ-bond system (inductive component) and through the π-bond system (resonance component). Taft has shown[2] that when resonance involving the benzene ring can occur between the substituent and the reactive centre the Hammett σ_p and σ_m values must be corrected, or alternatively an equation of the type

$$\lg \frac{k_{sub}}{k_0} = \rho + \psi$$

must be used, where Ψ is a parameter which characterises the resonance effect, even though the use of Hammett's σ parameter as a purely polar parameter is no longer justified.

Unfortunately, in radical reactions such as the abstraction of hydrogen from ring-substituted toluenes we can expect the substituents to show an additional resonance effect, due to delocalisation of the unpaired electron in the resulting free radical:



(3)

Brown and Okamoto[3] have proposed a different set of constants for the substituents, based on their study of the rates of hydrolysis of substituted cumyl chlorides (denoted σ^+). Since tertiary carbonium ions are formed as intermediates in these reactions, the contribution of the resonance effect to σ^+ is much larger than with the normal (σ) Hammett constants. Therefore the σ^+ scale may prove very useful in studies of free-radical reactions.

a. *Application to free-radical substitution reactions*

During the 1950's it was shown that the Hammett equation is applicable (in principle) to free-radical reactions such as the abstraction of hydrogen from toluenes by bromine[4] and chlorine[5,6] atoms, the reactions of peroxide

radicals with cumene derivatives[7], radical copolymerisation reactions[8], etc. (However, most of this work is now only of historical interest, because our understanding of reaction mechanisms has become much more precise since the advent of such analytical techniques as gas–liquid chromatography and NMR spectroscopy.) Shortly after the publication of Brown and Okamoto's paper[3], Russell[9] proposed a comparison of the correlations σ and σ^+ in the study of the transition-state structure in free-radical substitution reactions of the type

$$R^{\cdot} + R'X \rightarrow RX + R''. \qquad (4)$$

According to Russell, the transition state of these reactions can be treated as the sum of two basic structures:

$$\underset{(I)}{[R^{\cdot}X:R']} \rightleftarrows \underset{(II)}{[R^{\delta-}:X^{\delta+}R']}.$$

If the radical R$^{\cdot}$ has a high reactivity, the structure of the transition state should be (by Hammond's postulate[10]) similar to that of the reactants, i.e. the contribution of structure (I) should predominate. Conversely, in the reactions of low-activity free radicals the transition state should be similar to structure (II), since the passage of these systems over the energy barrier corresponds essentially to a weakening of the R′–X bond and therefore the structure of the transition state is similar to that of the products. Hence the rate constants of active radicals should show a better correlation with the σ parameters (since the resonance effect of R′ in structure (I) is negligible), and the rate constants of relatively inactive radicals should correlate better with σ^+ (since R′ in structure (II) has an unpaired electron, and the resonance in it should be approximately the same as in the free radical).

Hammett's equation has been used mostly in studies of free-radical substitution reactions (Table 1). As the Table shows, most of the publications deal with reactions in which hydrogen is abstracted from toluene derivatives, but Hammett's equation has been used also in studies of hydrogen abstraction from derivatives of ethylbenzene, cumene, allylbenzene, benzyl ethers, benzaldehyde, t-butylbenzene, phenols, neopentylbenzene, anisole, diphenylmethane, thiophenol and aniline, and also reactions in which iodine and chlorine are abstracted from derivatives of iodobenzene and benzenesulphonyl chloride.

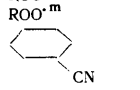
Russell's hypothesis has been tested on many reactions. In 1963 Howard and Ingold[55] concluded, from a critical analysis of existing data, that for the vast majority of reactions (including those involving active radicals such as Cl$^{\cdot}$ and $(CH_3)_3CO^{\cdot}$) a more precise correlation is obtained with the σ^+ constants. However, subsequent work has produced many examples of reactions in which correlation with the σ constants is better than with σ^+ (see Table 1).

The numerical value of the proportionality constant ρ in Hammett's equation depends mainly on the structure of the transition state and on the polarity of the free radical. The effect of substituents in the substrate molecule can be expected to be smaller with structure (I) than with structure (II): in other words, ρ should decrease on going from (II) to (I) if all other factors are the same. On the other hand, any increase in the electronegativity of the free radical should increase the rate of reaction with compounds possessing electron-donating substituents. As Table 1 shows, $\rho \leqslant 0$ for all hydrogen abstraction reactions. Since in Hammett's scale the constants for electron-donor substituents are negative and those for electron-acceptor substituents are positive[1,2], it follows that all the radicals examined either show electrophilic properties in these reactions or (as in the case of $CH_3^{\cdot}$) they do not show a polar effect. However, CuCl and $C_6H_5^{\cdot}$ behave as nucleophiles ($\rho > 0$) in halogen abstraction reactions[61,62]. In keeping with this point of view, a qualitative dependence of ρ on the electronegativity of the free radicals is often observed. For example, the absolute value of ρ increases in the series $CH_3^{\cdot} < C_6H_5^{\cdot} < HOOCCH_2^{\cdot} < CCl_3^{\cdot}, Br^{\cdot}$, i.e. in the same sense as the electronegativity of these radicals. However, the dependence is not universal, since the value of ρ is determined by two factors (see above). Thus, $|\rho_{Cl}| < |\rho_{Br}|$, in spite of the fact that chlorine is more electronegative than bromine.

Table 1. Application of Hammett's equation to free-radical substitution reactions.

Radical	Substrate	Temp., °C	Solvent	ρ[a]	r[c]	ρ^+[b]	r[c]	References
$CH_3^{\cdot}$	H—$CH_2C_6H_4X$	~110	—	0	—	0	—	11
$CH_3^{\cdot}$	ditto	100	—	−0.121±0.062		−0.139±0.045		12
$CCl_3^{\cdot}$	» »	50	—	—	—	−1.46	—	13
$C_6H_5^{\cdot}$	» »	60	CCl_4	0	—	0	—	14
ditto	» »	100	ditto	−0.5[d]	—			15
» »	» »	60	» »	−0.4	—	−0.3	—	17
p-$CH_3C_6H_4^{\cdot}$	» »	60	» »	−0.1	—	−0.1	—	17
p-$BrC_6H_4^{\cdot}$	» »	60	» »	−0.32	—	−0.25	—	17
p-$O_2NC_6H_4^{\cdot}$	» »	60	» »	−0.589	—	−0.437	—	17
$HOOCCH_2^{\cdot}$	» »	130	CH_3COOH	—	—	−0.63	—	18
Cl$^{\cdot}$	» »	40	CCl_4	−0.76±0.06	—	−0.66±0.02	—	19
ditto	» »	60	C_6H_6	−0.977	0.988	—	—	20
» »	» »	80	C_6H_5Cl	−0.779	0.993	—	—	20
» »	» »	80	C_6H_5CN	−0.530	0.986	—	—	20
» »	» »	80	$C_6H_5NO_2$	−0.498	0.998	—	—	20
» »	» »	60	CCl_4	−0.480	0.997	—	—	20
$ClSO_2^{\cdot}$	» »	40	ditto	−0.56±0.02	0.98	−0.47±0.09	0.81	21
Br$^{\cdot}$	» »	80	» »	−1.68	0.945	−1.38	0.977	22
ditto	» »	80	» »	—	—	−1.23±0.13	0.970	23
» »	» »	80	C_6H_6	—	—	−1.39±0.03	—	24
» »	» »	19	» »	—	—	−1.78±0.06	—	24
» »	» »	60	» »	−0.693	0.996	—	—	20
» »	» »	80	C_6H_5Cl	−1.662	0.989	—	—	20
» »	» »	80	C_6H_5Br	−1.639	0.981	—	—	20
» »	» »	60	$C_6H_5CF_3$	−1.048	0.994	—	—	20
» »	» »	80	$C_6H_5NO_2$	−0.334	0.998	—	—	20
$(CH_3)\dot{C}O^{\cdot} + Cl^{\cdot}$	» »	40	—	−0.821±0.008		−0.695±0.015	—	25
ditto	» »	39.5	C_6H_6	−0.750	0.984	−0.599	0.953	26
» »	» »	40	CCl_4	−0.86	0.972	−0.68	0.999	27
» »	» »	40	CCl_4, C_6H_6	−0.76	0.991	−0.64	0.974	28
$(CH_3)_3CO^{\cdot}$	» »	45	$CFCl_2CF_2Cl$	−0.40	0.977	−0.35	0.989	29
ditto	» »	45	C_6H_5Cl	−0.36	0.953	−0.32	0.973	29
» »	» »	45	CH_3CN	−0.43	0.955	−0.39	0.994	29
» »	» »	40	C_6H_5Cl	−0.386	0.989	−0.345	0.999	30
$(C_6H_5)_2\dot{C}—\dot{O}$	» »	22	—	—	—	−1.16[e]	0.981	31

Table 1 (contd.)

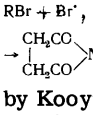
Radical	Substrate	Temp., °C	Solvent	ρ[a]	r[c]	ρ^+[b]	r[c]	References
Indoxy-phenyl	H—NHC$_6$H$_4$X	30	C$_6$H$_4$(CH$_3$)$_2$	−2.53	—	—	—	32
(CH$_2$)$_5$ṄH·	ditto	20	H$_2$SO$_4$—CH$_3$COOH	−1.5	—	−1.36[e]	—	33
ĊCl$_3$	H—CH(CH$_3$)C$_6$H$_4$X	80	CCl$_4$	—	—	−0.53[e]	0.98	34
Br·	ditto	80	ditto	—	—	−0.69±0.03	0.99	35
ClSO$_2$·	» »	40	» »	−0.49±0.02	0.98	−0.40±0.05	0.89	21
ĊCl$_3$	H—C(CH$_3$)$_2$C$_6$H$_4$X	70	» »	−0.89±0.04	0.988	−0.67±0.04	0.984	36
Br·	ditto	70	» »	−0.38±0.02	0.974	−0.29±0.04	0.954	35
XC$_6$H$_4$Ċ(CH$_3$)$_2$OO·[e]	» »	60	CH$_3$COOH, C$_6$H$_5$Cl	—	—	−0.41±0.01[e]	—	19
C$_6$H$_5$Ċ(CH$_3$)$_2$OO·	» »	30	C$_6$H$_5$Cl	−0.35±0.07	—	−0.29±0.04	—	37
ĊCl$_3$	H—CH[C(CH$_3$)$_3$]C$_6$H$_4$X	70	—	−1.24±0.05	0.960	−0.94±0.04	0.980	38
Br·	ditto	70	—	−0.96±0.04	0.942	−0.75±0.03	0.986	38
ĊCl$_3$	H—CH(CH=CH$_2$)C$_6$H$_4$X	69.5	CCl$_4$	−0.58±0.03[d]	0.99	−0.39±0.03	0.94	39
Br·	ditto	69.5	ditto	—	—	−0.76±0.03	0.99	39
ditto	» »	80	» »	—	—	−0.68±0.04[e]	0.992	40
» »	H—CH(C$_6$H$_5$)C$_6$H$_4$X	80	» »	−0.93±0.04	0.991	−0.62±0.06	0.980	40
» »	То же	77	» »	−0.97	0.990	−0.72	0.973	41
» »	H—CH(COC$_6$H$_5$)C$_6$H$_4$X	80	» »	−0.92±0.02	0.997	−0.72±0.06	0.980	40
» »	H—CHXC$_6$H$_5$	77	» »	—	—	−0.246[e]	0.95	42
ĊCl$_3$	H—CH(OCH$_3$)C$_6$H$_4$X	80	» »	—	—	−0.36[e]	0.99	43
Br·	ditto	80	» »	—	—	−0.35[e]	0.99	43
ditto	» »	40	» »	−0.48±0.04[g]	0.988	−0.43±0.03	0.995	21
» »	H—C(OCH$_3$)$_2$C$_6$H$_4$X	40	» »	—	—	−0.38[e]	0.99	43
ĊCl$_3$	ditto	80	» »	—	—	−0.18±0.01[e]	0.99	34
Br·	H—CH(OCH$_2$C$_6$H$_5$)C$_6$H$_4$X	80	» »	−0.19	0.942	−0.12	0.947	44
C$_6$H$_5$COO·	ditto	80—90	—	−0.957±0.047	—	−0.647±0.016	—	45
Br·	H—C(C$_6$H$_5$)(OCH$_3$)C$_6$H$_4$X	80	CCl$_4$	—	—	0.0	—	35
ĊCl$_3$	ditto	80	ditto	−0.20±0.02	0.947	−0.12±0.02	0.957	34
» »	H—COC$_6$H$_4$X	80	» »	−0.74	0.994	−0.67	0.951	46
ĊCl$_3$SO$_2$·	ditto	80	» »	−0.54±0.04	0.999	−0.46±0.03	0.979	47
ClSO$_3$·	» »	40	» »	−0.53±0.03	0.981	−0.30±0.07	0.890	48
Cl·	H—CH$_2$Ċ(CH$_3$)$_2$C$_6$H$_4$X	70	C$_6$H$_5$Cl	−0.44±0.01[h]	0.995	—	—	49
(CH$_3$)$_3$CO·	H—CH$_2$OC$_6$H$_4$X	45	CFCl$_2$CF$_2$Cl	−0.41				50
ditto	H—OC$_6$H$_4$X	122	C$_6$H$_5$Cl	—	—	−0.74[i]	—	51
» »	ditto	122	CCl$_4$	—	—	−1.19[i]	—	51
	» »	24	C$_6$H$_6$	—	—	−2.72[j]	—	52
DPPH	H—OC$_6$H$_4$X	20	CCl$_4$	−6.4±0.3	—	−4.54±0.064[k]	—	53
DPPH	ditto	30	C$_6$H$_6$	−3.22±0.16	—	−2.77±0.09[k]	—	54
ROO·	» »	65	C$_6$H$_5$CH=CH$_2$	—	—	−1.585±0.016	—	55
—CH$_2$ĊH(OCOCH$_3$)	» »	50	—	—	—	−1.52[e]	—	56
(CH$_3$)$_3$CO·	H—OC$_6$H$_2$(OC$_4$H$_9$)$_3$	122	CCl$_4$	—	—	−0.86[i]	—	51
ditto	» »	122	C$_6$H$_5$Cl	—	—	−0.78[i]	—	51
ROO·[l]	» »	65	—	—	—	−1.36±0.043	—	57
ROO·[m]	» »	65	—	—	—	−1.12	—	57
	H—SC$_6$H$_4$X	110	C$_6$H$_5$CH$_3$	−0.4	—	—	—	58
—CH$_2$Ċ(CH$_3$)COOCH$_3$	ditto	45	—	−0.23±0.1[k]	—	—	—	59
—CH$_2$ĊH(OCOCH$_3$)	H—NHC$_6$H$_4$X	50	—	—	—	−0.6[e]	—	60
C$_6$H$_5$·	I—C$_6$H$_4$X	60	CCl$_4$	0.57	0.946	—	—	61
CuCl	Cl—SO$_2$C$_6$H$_4$X	110	CH$_2$=CHC$_6$H$_5$, CH$_3$CN	0.565	—	—	—	62

a) Correlation with σ. b) Correlation with σ^+. c) Correlation coefficient. d) Correlation with σ^0 [16]; p-NO_2 and p-CN showed large discrepancies and were not used in the calculation. e) Correlation with σ worse than with σ^+. f) p-$(CH_3)_3CO$ and p-C_6H_5O not included in the correlation. In the determination of the rate constants for hydrogen abstraction these constants had been assumed independent of the structure of X in $X-C_6H_4C(CH_3)_2OO^\cdot$, but this assumption is incorrect[37]. g) p-CH_3O not included in the correlation. h) m-NO_2 not included in the correlation. i) These values are approximate, due to the side reaction $XC_6H_4O^\cdot + HOC_6H_4Y \rightarrow XC_6H_4OH + {}^\cdot OC_6H_4Y$. j) Correlation satisfactory only for *meta*-substituents. k) Recalculated by Harvey et al.[49] 1) Oxidation of decalin. m) Oxidation of styrene. Earlier results, which were later disproved or to which substantial corrections had to be applied, are not considered in Table 1.

An accurate determination of the value of ρ can help to establish the reaction mechanism. In 1953 Kooyman and coworkers[4] suggested that succinimidyl is formed in the reactions between bromosuccinimide and hydrocarbons, and acts as a chain carrier. They based their suggestion on the fact that the value of ρ in the Hammett equation for the bromination of substituted toluenes by bromosuccinimide was found to be −1.55, i.e. significantly different from the value −0.97 which applies to bromination by molecular bromine. On the other hand, later work showed[22-24] that the parameter ρ does not depend on the structure of the organic part of the *N*-bromoimide, and furthermore that the same value of ρ is obtained for bromination with an excess of molecular bromine. This observation suggests that the chain-propagating radical in bromination reactions with *N*-bromoimides is a bromine atom:

$$Br^\cdot + RH \rightarrow HBr + R^\cdot, \quad (5)$$

$$R^\cdot + Br_2 \rightarrow RBr + Br^\cdot, \quad (6)$$

$$HBr + \text{ } \rightarrow \text{  } + Br_2. \quad (7)$$

The lower value of ρ found by Kooyman and coworkers for reactions with molecular bromine is ascribed to the

fact that reaction (5) is reversible in the absence of excess bromine.

In 1967, the mechanism of the reaction between t-butyl hypochlorite and aromatic hydrocarbons was re-examined[29] in a similar way, because the value of ρ in reactions between substituted toluenes and $(CH_3)_3CO^{\cdot}$ radicals formed by the decomposition of di(t-butyl)peroxyoxalate was much lower than in reactions with t-butyl hypochlorite[25-28] (see Table 1). It follows that the chains are propagated mainly by chlorine atoms in the reactions with t-butyl hypochlorite. This conclusion was subsequently confirmed by Walling and McGuiness[30].

On going to more reactive substrates the absolute value of ρ decreases, as is to be expected from an increased contribution of structure (I) (see p. 218) to the transition state of the reaction†. Therefore, the reactions of $Br^{\cdot}$ and $CCl_3^{\cdot}$ with derivatives of cumene, diphenylmethane, and benzaldehyde show a better correlation with ρ than with ρ^+ [40,41,46-48].

Recently, Japanese workers have used a two-parameter Hammett equation containing the resonance constant E_R in their studies of various chain carriers—substituted cumenes in the polymerisation of styrene, *p*-chlorostyrene, *p*-methoxystyrene, methyl methacrylate[63-65,70] and substituted toluenes, benzaldehydes, and aliphatic–aromatic ketones in the polymerisation of styrene and methyl methacrylate[66-69]:

$$\lg \frac{k_{sub}}{k_0} = \rho\sigma + \gamma E_R \,. \qquad (8)$$

However, Taft himself had shown[2] that the insertion of Hammett's σ into Eqn.(8) cannot give a correct value of the resonance constant, because σ characterises the resonance as well as the polar effect of the substituent. Hence, it is better to use Taft's constants σ^0 [16] as the polar parameters in Eqn.(8), since these constants relate only to the inductive effect of the substituent.

Also, it was recently shown[28] that the methoxy group reacts with free radicals at about the same rate as the methyl group. Therefore, the rate constants of the reactions of *m*- and *p*-methoxytoluene cannot be included when correlation equations are set up for substituted toluenes. It should be noted that the point for *p*-methoxytoluene shows the greatest deviation from the line in plots[63-70] of Hammett's Eqn. (1). Lastly, deviations from Hammett's Eqn. (1) may arise from solvent effects[20] in concentrated solutions. Thus, further work is needed before the resonance constants of Eqn. (8) can be evaluated with confidence.

b. *Application to free-radical addition reactions*

During the addition of free radicals to benzene derivatives the conjugated aromatic system is converted into a cyclohexadienyl double-bond system. Therefore, Hammett's σ values (which apply to systems in which the aromatic character is not disturbed) cannot be used in this case. Furthermore, any study of reactions of this type must include, in addition to the usual assessment of the reactivity of the substrate, the partial rate constants for addition at the *para*-, *meta*-, and *ortho*- positions of each benzene derivative, because the isomeric composition of the products depends on the nature of the substituent. A full kinetic analysis of this type has been attempted only for relatively few reactions[71-75].

It has been shown that the Hammett equation is obeyed by the rate constants for the addition of the radicals $C_6H_5^{\cdot}$, $p\text{-}CH_3C_6H_4^{\cdot}$, $p\text{-}CH_3OC_6H_4^{\cdot}$, $p\text{-}ClC_6H_4^{\cdot}$, and $p\text{-}O_2NC_6H_4^{\cdot}$ to the *meta*-position, the sign changing from positive to negative on going from radicals with electron-donating to radicals with electron-accepting substituents (see Table 2). The Hammett equation can be applied also to reactions in which the radicals cyclo-$C_6H_{11}^{\cdot}$, $C_6H_5COO^{\cdot}$, $p\text{-}CH_3C_6H_4COO^{\cdot}$, $p\text{-}O_2NC_6H_4COO^{\cdot}$, $(CH_3)_2COCOO^{\cdot}$, and $C_6H_5C{\equiv}C^{\cdot}$ are added at the *para*- and *meta*-positions. However, the rate constants for the addition of aryl radicals at the *para*-position do not appear[71] to follow Hammett's equation. Ito and coworkers[71] believe that the deviations from Hammett's equation can be attributed to the resonance effect. They calculate the resonance parameters by using the fact that $\rho_{para} = \rho_{meta}$. The resonance parameters for attack in the *ortho*-position were determined in a similar way. The objections to the use of the ordinary σ constants for the substituents when the Hammett equation has a resonance term are discussed above‡.

Martin and Gleicher[76] showed that the Hammett equation is applicable to the rate constants for the addition of $CCl_3^{\cdot}$ to substituted allyl- and 3-butenylbenzenes, the proportionality constants ρ taking the values −0.29 and −0.20 respectively (Table 2). They consider these values to be too high, and they point out that the trichloromethyl radical can form complexes with aromatic substrates. Cadogan and Sadler[77] found a correlation between the rate constants for the addition of $CCl_3^{\cdot}$ and $HOOCCH_2S^{\cdot}$ radicals to substituted stilbenes and the σ^+ constants of the substituents, but this correlation was limited to a small number of olefins.

In 1948 Walling and coworkers had pointed out[8] that the rate constants for the addition of a polystyrenyl radical to ring-substituted styrenes obey the Hammett equation. Their calculations were based on the copolymerisation constants. More recently, the Hammett equation was shown to be applicable to the rate constants for the polymerisation of substituted styrenes[78]. An attempt to correlate the reactivities of ethyl-(α-substituted benzyl)-acrylates towards copolymerisation with styrene and methyl methacrylate gave a curved Hammett plot[82]. This was ascribed[82] to the resonance effect of the substituents.

In all the examples of free-radical substitution and addition reactions considered so far, the substituents are in the substrate molecules. Reactions between substituted aryl radicals and unsubstituted substrates are difficult to study. The first demonstration of the possible use of Hammett's equation for systems of this type was based[17]

† Exceptionally, the value of ρ for the reaction of $CCl_3^{\cdot}$ with derivatives of toluene[34] (−0.53) is smaller than the values for the reactions of the same radical with derivatives of cumene[36] (−0.67) and neopentylbenzene[38] (−0.94). According to Totherow and Gleicher[38], this is because the reaction of $CCl_3^{\cdot}$ is made more selective by steric hindrance in the latter two cases.

‡ Recent work has raised additional doubts about the correctness of this approach[71]. Thus, the rate constants for the addition of phenyl radicals in both the *para*- and the *meta*-position ($\rho = 0.0$) were found[73] to satisfy the Hammett equation. However, Japanese workers[80,81] find that the value of ρ in the Hammett equation for the addition of $C_6H_5^{\cdot}$ in the *para*-position depends on the method of generating the phenyl radicals. They ascribe this effect to the influence on the measured addition rate constants of the rate of the reaction

$$C_6H_5C_6H_5Y^{\cdot} + X^{\cdot} \rightarrow C_6H_4C_6H_4Y + HX$$

where the structure of X depends on the method of generating the phenyl radicals.

Table 2. Application of Hammett's equation to free-radical addition reactions.

Radical	Substrate	Product	Temp., °C	ρ	Refs.
$C_6H_5^{\cdot}$	C_6H_5X	m-$C_6H_5C_6\dot{H}_5X$	20	0.05	71
p-$CH_3C_6H_4^{\cdot}$	ditto	m-(p-$CH_3C_6H_4$)$\dot{C}_6H_5X$	20	0.03	71
p-$CH_3OC_6H_4^{\cdot}$	» »	m-(p-$CH_3OC_6H_4$)$\dot{C}_6H_5X$	20	0.09	71
p-$ClC_6H_4^{\cdot}$	» »	m-(p-ClC_6H_4)$\dot{C}_6H_5X$	20	−0.27	71
p-$O_2NC_6H_4^{\cdot}$	» »	m-(p-$O_2NC_6H_4$)$\dot{C}_6H_5X$	20	−0.81	71
$C_6H_5COO^{\cdot}$	» »	p-and$m$-$C_6H_5COO\dot{C}_6H_5X$	60	−1.61±0.044[a]	72
p-$CH_3C_6H_4COO^{\cdot}$	» »	p-and$m$-(p-$CH_3C_6H_4COO$)$\dot{C}_6H_5X$	60	−1.28±0.047[a]	72
p-$O_2NC_6H_4COO^{\cdot}$	» »	p-and$m$-(p-$O_2NC_6H_4COO$)$\dot{C}_6H_5X$	60	−2.52±0.058[a]	72
$C_6H_5C{\equiv}C^{\cdot}$	» »	p-and$m$-$C_6H_5C{\equiv}C\dot{C}_6H_5X$	20	−1.56	73
$(CH_3)_2CHOCOO^{\cdot}$	» »	p-and$m$-$(CH_3)_2CHOCOO\dot{C}_6H_5X$	60	−2.27±0.03[a]	74
cyclo-$C_6H_{11}^{\cdot}$	» »	p-and$m$-$C_6H_{11}\dot{C}_6H_5X$	90	1.1±0.1[b]	75
$CCl_3^{\cdot}$	$CH_2{=}CHCH_2C_6H_4X$	$CCl_3CH_2\dot{C}HCH_2C_6H_4X$	69.5	−0.29±0.02[c]	76
ditto	$CH_2{=}CH(CH_2)_2C_6H_4X$	$CCl_3CH_2\dot{C}H(CH_2)_2C_6H_4X$	69.5	−0.20±0.02[c]	76
» »	$C_6H_5CH{=}CHC_6H_4X$	$CCl_3CH(C_6H_5)\dot{C}HC_6H_4X$	105	−0.7[a)]	77
$HOOCCH_2S^{\cdot}$	ditto	$HOOCCH_2SCH(C_6H_5)\dot{C}HC_6H_4X$	105	−0.4[a)]	77
$-CH_2\dot{C}HC_6H_5$	$CH_2{=}CHC_6H_4X$	$-CH_2CH(C_6H_5)CH_2\dot{C}HC_6H_4X$	60	0.51	8
$-CH_2\dot{C}HC_6H_4X$	$CH_2{=}CHC_6H_4X$	$-CH_2CH(C_6H_4X)CH_2\dot{C}HC_6H_4X$	60	0.60	78
$XC_6H_4^{\cdot}$	$CH_2{=}CHC_6H_5$	$XC_6H_4CH_2\dot{C}HC_6H_5$	20	0.95[d)]	79
ditto	$CH_2{=}C(CH_3)COOCH_3$	$XC_6H_4CH_2\dot{C}(CH_3)COOCH_3$	20	0.46[d)]	79
» »	$CH_2{=}CHCOOCH_3$	$XC_6H_4CH_2\dot{C}HCOOCH_3$	20	0.38[d)]	79
» »	$CH_2{=}C(CH_3)CN$	$XC_6H_4CH_2\dot{C}(CH_3)CN$	20	0.35[d)]	79

a) Correlation with σ^+. b) Correlation with σ worse than with σ^+. c) Correlation with σ^0. d) ρ for the monomer minus ρ for acrylonitrile.

on the substitution reactions of *p*-methyl-, *p*-bromo, and *p*-nitrophenyl radicals with *p*-methoxytoluene ($\rho = +1$) and *p*-nitrotoluene ($\rho = +0.4$). Dickerman and coworkers[79] have shown that Hammett's equation is obeyed in reactions involving the addition of substituted phenyl radicals to styrene, methyl methacrylate, methyl acrylate, and acrylonitrile. Similarly, Yamamoto and Otsu[70] have applied the Hammett equation to the rate constants for the abstraction of hydrogen from cumene-substituted polystyrenyl radicals with different *para*-substituents, and Prokof'ev and coworkers[83] have applied it to the rate constants for the reactions of 2,6-di-t-butyl-4(4-X-phenyl)phenoxyls with t-butyl peroxide.

2. The Taft Equation

The Taft equation, which has been used to study addition reactions of aliphatic compounds, is formally similar to the Hammett equation:

$$\lg \frac{k_{sub}}{k_0} = \rho^* \sigma^* \cdot \quad (9)$$

However, the essential difference between Eqn. (9) and the Hammett equation is that the σ^* constants are related exclusively to the polar effect of the substituents[2].

Until quite recently, the Taft equation had been used very seldom in studies of free-radical reactions. Taft himself quotes[84] only one example of the application of his equation to a free-radical reaction (the reaction between sodium atoms and alkyl chlorides[85]). In 1962 it was shown in the writer's laboratory[86] that the chain transfer constants in the telomerisation of ethylene with chloro- and bromochloromethane are very accurately described by Eqn. (9). (These constants, when the chain length is $n \geq 3$, are essentially the relative rate constants for the abstraction of hydrogen and bromine atoms by n-alkyl radicals, and for the removal of bromine from bromochloromethane by methyl radicals[87]). It is worth pointing out that the rate constants covered a range of 10^6, and the proportionality constant ρ^* lay within the range 2.33 ± 0.04 irrespective of the nature of the functional group.

We then measured the chain transfer constants for a number of other chloro- and bromochloromethanes, and refined the values previously obtained[88-90]. All the results agreed satisfactorily with Eqn. (9). We also showed that the experimental chain transfer constants for the telomerisation of ethylene with chloroform (involving breaking a C−Cl bond) and with chlorobromo- and dibromomethane (involving breaking a C−H bond) are in good agreement with the values predicted by the Taft equation.

In 1962 Patmore and Gritter[97] applied Eqn. (9) to the rate constants for the abstraction of hydrogen from derivatives of cyclohexane by the $(CH_3)_3CO^{\cdot}$ radical, but they amounted some grave difficulties. In recent years the equation has been applied to many other free-radical substitution and addition reactions (Table 3).

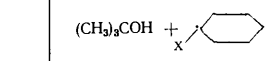
Gleicher and coworkers report[99,100] that in reactions with substituted adamantanes the inductive effect of the substituent is apparently transmitted to the reaction centre through space rather than through the carbon−carbon bond system. They calculated the relative rate constants for the reactions with $CCl_3^{\cdot}$ and $Br^{\cdot}$, using the Kirkwood–Westheimer model[102] of the electrostatic effect, and assuming that the positive charge in the transition state is unity. The calculated values turned out to be much larger than the observed rate constants, but their internal consistency was very good if the charge of the transition state was assumed to be fractional and equal to 0.12 ± 0.03 for the reactions with $CCl_3^{\cdot}$ and 0.17 ± 0.03 for the reactions with $Br^{\cdot}$. More recent work from the same laboratory[49] has confirmed that free-space transmission of the inductive effect plays an important part in the free-radical chlorination of substituted t-butylbenzenes.

In general, the rate constants of free-radical reactions should obey an extended form of the Taft equation[2]:

$$\lg \frac{k_{sub}}{k_0} = \rho^* \sigma^* + r^* \sigma^r + \delta E_s \cdot \quad (10)$$

In this equation σ^r and E_S are constants for the substituents, characterising their resonance and steric effects, and r^*

Table 3. Application of Taft's equation to free-radical reactions.

Radical	Substrate	Product	Temp., °C	ρ^*	Refs.
$R(CH_2CH_2)_{\geqslant 3}^{\cdot}$	$H-CH_xCl_{3-x}$	$R(CH_2CH_2)_{\geqslant 3}-H + {}^{\cdot}CH_xCl_{3-x}$	70—100	2.33±0.03	86
ditto	$Br-CH_xHal_{3-x}$	$R(CH_2CH_2)_{\geqslant 3}-Br + {}^{\cdot}CH_xHal_{3-x}$	100	2.32±0.03	88—90
$CH_3^{\cdot}$	$Br-CH_xCl_{3-x}$	$CH_3Br + {}^{\cdot}CH_xCl_{3-x}$	65	2.33±0.03	86a
e_{aq}^- b	Hal—X	$Hal^- + X^{\cdot}$	20	c	91
$Cl^{\cdot}$	$H-CH_2X$	$HCl + {}^{\cdot}CH_2X$	20	−1.25	92
ditto	ditto	ditto	40	−0.85	92—94
» »	» »	» »	100	−1.00	95
» »	H—CHClX	HCl + ·CHClX	20	−0.83	92
» »	$H-CCl_2X$	$HCl + {}^{\cdot}CCl_2X$	20	−0.49	92
$(CH_3)_3CO^{\cdot}$	$H-CH_2X$	$(CH_3)_3COH + {}^{\cdot}CH_2X$	40	−0.69	96
ditto		$(CH_3)_3COH +$ 	135	−0.43	97
$(C_2H_5)_3Si^{\cdot}$	$Cl-CCl_2X$	$(C_2H_5)_3SiCl + {}^{\cdot}CCl_2X$	80	0.29	98
$C_6H_5(CH_3)_2Si^{\cdot}$	ditto	$C_6H_5(CH_3)_2SiCl + {}^{\cdot}CCl_2X$	80	0.26	98
$CCl_3^{\cdot}$		$CHCl_3 +$	40	−0.40±0.04 (r=0.980)	99
$Br^{\cdot}$	ditto	$HBr +$	40	−0.59±0.04 (r=0.992)	100
$CCl_3^{\cdot}$	$CH_2=CHX$	$CCl_3CH_2\dot{C}HX$	69.5	−0.42 (r=0.99)	101
$-CH_2\dot{C}HC_6H_5$	$CH_2=CHCOOX$	$-CH_2CH(C_6H_5)CH_2\dot{C}HCOOX$	60	0.56	103
ditto	$CH_2=C(CH_3)COOX$	$-CH_2CH(C_6H_5)CH_2\dot{C}(CH_3)COOX$	60	0.30	104
» »	$CH_2=CHCOSH$	$-CH_2CH(C_6H_5)CH_2\dot{C}HCOSX$	60	0.28	105
$-CH_2\dot{C}(CH_3)COOX$	$CH_2=C(CH_3)COOX$	$-CH_2C(CH_3)(COOX)CH_2\dot{C}(CH_3)COOX$	30	0.70±0.18	106

a) Calculated from the results of Evans and Szwarc[87]. b) Hydrated electron. c) Published plot shows unacceptable scatter of experimental points.

and δ are the appropriate proportionality constants. Two partial expressions of Eqn. (10) are of practical importance:

$$\lg\frac{k_{sub}}{k_0} = \rho^*\sigma^* + r^*\sigma^r, \qquad (11)$$

$$\lg\frac{k_{sub}}{k_0} = \rho^*\sigma^* + \delta E_s. \qquad (12)$$

The first application of Eqn. (11) to the study of free-radical reactions was reported in an investigation[107] of the distribution of isomers in the products of the liquid-phase chlorination of aliphatic acids, esters, and nitriles. The constant ρ^* was found to be −0.212, and the hyperconjugation parameter h was also evaluated (h = 0.114, where $h = \frac{r^* \cdot \sigma^r_{CH_3}}{3}$). However, although the correlation was fairly precise, the method of calculation is open to criticism, since the authors allowed for the hyperconjugation with the methyl substituents but ignored the resonance effect of the COOH, $COOCH_3$, and CN groups. In 1965 the writer applied Eqn. (11) to the rate constants for the abstraction of iodine from alkyl iodides by alkyl radicals[108,109]. The use of the two-parameter Eqn. (11) in studies of free-radical reactions is discussed below in greater detail.

Martin and Gleicher showed[101] that the rate constants for the addition of the trichloromethyl radical to substituted olefins obey Taft's equation in its simplest form (Eqn. (9)). Similar conclusions were made for the rate constants of the addition of the polystyrenyl radical to acrylates[103], methacrylates[104], and thioacrylates[105], and also the addition of the poly(methyl methacrylate) radical to methacrylates[106], the substituents being in the alcoholic part of the monomer molecule. However, Eqn. (9) could not be applied to the rate constants of the reactions between free radicals and silicon-containing olefins of general formula $CH_2=CHSiX_1X_2X_3$[110,111], because these reactions involve large steric and resonance effects. Similarly, the rate of addition of the polystyrenyl radical to α-substituted methyl acrylates is determined mainly by the steric effect of the substituents[112].

3. The Alfrey–Price and the Bamford Equations

The Alfrey–Price[113] and the Bamford[114-116] equations were put forward to describe reactivity in radical polymerisation and copolymerisation reactions. A detailed description of these specialised branches of free-radical chemistry lies beyond the scope of the present review, and can be found in recent monographs[117-119]. We shall therefore confine ourselves to the use of the Alfrey–Price and the Bamford equation in quantitative descriptions of the reactivity of small radicals, with special reference to the recent work of Freidlina and Englin[120-123].

According to Alfrey and Price[113], the ratio of the rate constants for the polymeric radical $M_1^{\cdot}$ in copolymerisation reactions with the monomers M_1 and M_2 can be written in the form

$$r = \frac{k_{11}}{k_{12}} = \frac{Q_1}{Q_2}e^{-e_1(e_1-e_2)} \qquad (13)$$

where Q_1 and Q_2 are parameters which characterise the reactivity of M_1 and M_2, and e_1 and e_2 characterise the polar properties of these monomers.

Englin and Freidlina[120] proposed the use of a form of Eqn. (13), modified for chain transfer constants[124], to study the reactivity of telomeric radicals formed in the telomerisation of ethylene with carbon tetrachloride and chloroform. The Alfrey–Price scheme gives

$$C_\infty = \frac{Q_T}{Q_M}e^{-e_M(e_T-e_M)};\quad C_n = \frac{Q_T}{Q_M}e^{-e_n(e_T-e_M)} \qquad (14)$$

where C_n and C_∞ are the partial and the total chain transfer constant of the telogen; Q_M and Q_T are characteristic parameters for the reactivity of the monomer and the telogen; e_T, e_M, and e_n are the polar factors for the telogen, the monomer, and the telomeric radical of chain length n. Using Eqn. (14), Englin and Freidlina evaluated the e_n parameters for the radicals $CCl_3(CH_2CH_2)_n^{\cdot}$, where $n = 1-4$. They found that whilst the radical $CCl_3CH_2CH_2^{\cdot}$ is electrophilic ($e > 0$), the radicals with higher molecular weight acquire nucleophilic properties.

The same authors[121-123] later suggested the use of Bamford's equation[114-116]

$$\lg k_s = \lg k_{3T} + \alpha\sigma + \beta \qquad (15)$$

to study the reactivity of telomeric radicals and telogens, where k_S is the rate constant for the reaction between the radical and any substrate, k_{3T} is the rate constant for the reaction of the same radical with toluene, σ is a constant (analogous to Hammett's σ) which characterises the polar properties of the radical, and lastly α and β are constants characteristic of the substrate molecule.

For the case of chain transfer constants Eqn. (15) can be rewritten

$$\lg C_n = \sigma_n(\alpha_T - \alpha_M) + \beta_T - \beta_M. \qquad (16)$$

These equations were used to calculate σ_n for telomeric radicals in the telomerisation of ethylene, propylene, and vinyl chloride with carbon tetrachloride and chloroform. The σ_n values obtained varied in the right sense, reflecting the decrease in electrophilic character of the radicals both with increase of n and on going from vinyl chloride to ethylene and propylene.

III. CORRELATION WITH THE PARAMETERS OF QUANTUM CHEMISTRY

This review is not concerned with attempts to calculate the rate constants of free-radical reactions of the parameters of their Arrhenius equations by quantum-chemical methods. However, in addition to attempts at direct calculation of the kinetic parameters, considerable effort has been devoted to the comparison of the rate constants and activation energies of free-radical reactions with quantum-mechanical characteristics of the reactivity of the molecules and radicals. These correlations are similar in principle to those based on the use of empirical parameters (such as the constants for the substituents in the Hammett and Taft equations), but the use of quantum-mechanical parameters offers some additional advantages by giving a physical interpretation of the reactivity.

The most widely used among the quantum-mechanical correlation equations is that of Polanyi, which relates the activation energy to the enthalpy of free-radical reactions[125]:

$$\Delta E_{ac} = -\alpha\,\Delta\Delta H. \qquad (17)$$

In this equation ΔE_{ac} is the difference between the activation energies, and $\Delta\Delta H$ is the difference between the enthalpies of reactions of a given type; α is a proportionality constant. Semenov has stated[126] that this expression can be applied, to a first approximation, to the substitution reactions of most free radicals, and can be written in the form

$$E_{ac} = A - \alpha\,\Delta H \qquad (18)$$

As will be shown below (p. 228), the correctness of Eqn. (18) depends on the fact that the transition states of many free-radical reactions of the same type have very similar structures. However, in general, the proportionality constant α is a function of the reactivity of the free radical. The phenomenon has been discussed quantum-mechanically by Bagdasar'yan[119], who showed that α varies from 0 to 1 as the structure of the transition state varies from that of the reactants to that of the products.

Eqn. (17) and (18) have been applied to the abstraction of hydrogen by $CH_3^{\cdot}$ radicals ($\alpha = 0.49$ [127,128]), by Br ($\alpha = 0.86$ [129]), NF_2 ($\alpha \simeq 1$ [128]), and O ($\alpha = 0.36$ [130]). In Bagdasar'yan's calculations[119] for the reactions of $CH_3^{\cdot}$, $CF_3^{\cdot}$, and $D^{\cdot}$, α is found to be 0.38. All these examples apply to the reactions of radicals with aliphatic hydrocarbons only, because the Polanyi–Semenov equation is inappropriate[119] when the reactants contain any substituents other than alkyl groups. However, Eqns. (17) and (18) can be used in the study of reactions of a different type: for example, the abstraction of halogen atoms from alkyl halides by the $^{\cdot}SiCl_3$ radical[131], or the reactions of trifluoromethyl with halogens[132].

Zavitsas and Ehrenson[133] measured the ratio of the rate constants and the difference in the activation energies of the reactions of alkyl and cycloalkyl radicals with bromotrichloromethane and hypochlorites ($R(CH_2)_2COCl$), and evaluated the parameter α from Polanyi's equation. They found that for these radicals α is related to the stabilisation energy E_S by the expression

$$\alpha = 1.9 \cdot 10^{-3} \exp 0.28E_s. \qquad (19)$$

However, the experimental method used by these workers[133] is of doubtful validity, because recent work has shown[29,30] that appreciable amounts of chlorine are formed in reactions involving hypochlorites. Furthermore, we would have expected a linear relationship between α and E: the physical significance of the exponential relationship is not clear.

Eqns. (17) and (18) can be applied also to free-radical addition reactions[134]. Walling used[135] Eqn. (17) to determine the stabilisation energy of radicals formed during the addition of methyl radicals to vinyl acetate, vinyl ethyl ether, and methyl methacrylate.

The many "reactivity indices" which have been proposed for free-radical reactions can be divided into two groups: the parameters which define the polar (or inductive) effect, and those which define the resonance effect in reactions. In 1951 Eyring and coworkers[136] put forward a "semi-classical" approach to the evaluation of the inductive effect, based on a calculation by the MO method of the total charge on covalently bonded atoms[137]. It was shown that the free energy of the reaction between a sodium atom and chloromethanes increases in the same sense as the total charge on the chlorine atom[138]. This effect can be explained by assuming electron transfer from the sodium to the chlorine in the transition state of the reaction: increasing the number of chlorine atoms in the molecule leads to a decrease in the negative charge on the chlorine atom involved in the reaction, and hence to an increased rate of reaction. Thus, the chlorine atoms contribute a purely inductive effect. It is interesting to note that the same correlation equation applies to all the methyl halides investigated (CH_3Cl, CH_2Cl_2, $CHCl_3$, CCl_4, CH_3Br, CH_3I) if a correction for the different polarisabilities of the C–X bonds is applied.

Electron transfer in the transition state of the reaction between sodium and organic halides is confirmed by Wilson and Herschbach's observation of a correlation between the

electron capture coefficients and the rate constants of these reactions[139]. According to Polanyi[140], it is more correct to seek a correlation between the activation energy and the electron affinity for reactions of this type. However, both relationships point to the same mechanism.

The work of Szwarc and coworkers[141,142] bears a close similarity to the above investigations. These workers found an inverse relationship between the logarithm of the rate constants for the addition of the trifluoromethyl radical to methyl-substituted olefins and the ionisation potentials of the olefins[142]. This type of dependence is ascribed to the electron-donating properties of the methyl substituents. According to Stefani and coworkers[143] the logarithm of the rate constant for the addition of the cyclopropyl radical to olefins varies linearly with the ionisation potential of the olefins, which suggests that the cyclopropyl radical behaves nucleophilically.

In 1955 Coulson reported[144] a linear relationship between the logarithm of the rate constants for the addition of the methyl radical to aromatic compounds and the free valency index or the localisation energy of these compounds. This relationship has been widely discussed in the literature. The quantum-mechanical significance of these correlations has been considered in detail in monographs[119,145], and the work of Szwarc and coworkers up to 1958 is fully reviewed by the authors themselves[146]. The localisation energy of one of the π-electrons on the reactive centre decreases if the second electron can conjugate with the substituents of an unsaturated compound. Therefore, the correlation of the rate constants or activation energies with the localisation energies is evidence for the presence of a large resonance effect in these reactions.

Later work has revealed correlations between the localisation energies and the rate constants (and activation energies) for the reactions of the trifluoromethyl and the trichloromethyl radical with aromatic compounds[147,148], of hydrogen atoms with olefins[149] and hydrocarbons[150], and of the ethyl radical with olefins[151]. Chlenov and Basilevskii[152] studied the relationship between the rate constants for the reactions of the methyl, trifluoromethyl, and trichloromethyl radicals with aromatic compounds and the stabilisation energy, defined as the difference between the π-energies of the delocalised transition state and of the reactants. According to these workers, correlation with the stabilisation energy is more satisfactory than with the localisation energy when a large polar effect is present. Unruh and Gleicher[153] obtained a good correlation (correlation coefficient 0.977) between the rate constants for the abstraction of hydrogen from methyl-substituted aromatic compounds by the trichloromethyl radical and the difference between the π-bond energies of the resulting radical and of the reactant, calculated by the SCF LCAO MO method.

IV. ADDITIVE EMPIRICAL METHODS OF CALCULATING THE ACTIVATION ENERGIES AND THE RATE CONSTANTS OF FREE-RADICAL REACTIONS

Additive schemes for calculating by empirical methods the rate constants (and particularly the activation energies) of free-radical reactions have recently been developed to a remarkable degree. The activation energies of the logarithms of the rate constants are treated as empirical functions of a number of parameters which characterise the substrates and the radicals. Though similar to the correlation equations of the Hammett–Taft type, these methods differ essentially from those equations because the parameters on which they rely are not determined by reaction effects (polar, resonance, or steric), but by some specifically chosen components of the energy of the activated complex. The activation energies of radical reactions are treated as functions of the dissociation energies of the "activated" forms of the broken bond and the newly formed bond (i.e. the bonds in the activated complex[154]), expressed as sums of energy terms for the pair interactions of atoms in the activated complex[157], and also as functions of the dissociation energies of the real broken bond and of the newly formed bond[156]. §

These methods have been discussed in detail in a number of review articles, [154–156] and therefore we shall not dwell on them, except for the following observation. There can be no doubt of the reality of the various empirical relationships which have been reported. However, it is exceedingly difficult to define the region over which such relationships apply. Thus, Moin assumes[154] that in any free-radical substitution reaction

$$R^{\cdot} + R'X \rightarrow [R \ldots X \ldots R'] \rightarrow RX + R'^{\cdot} \qquad (20)$$

the dissociation energy of X... R′ in the activated complex is independent of the structure of the attacking radical R·. But this assumption is inconsistent with Hammond's postulate[10] that the structure of the activated complex (i.e. the transition state), and therefore also the dissociation energy of the X... R′ bond, varies from a structure close to that of the reactants (for very reactive R radicals) to a structure close to that of the reaction products (for relatively inactive R radicals).

Moin[154] correctly states that his relationships between activation energies and the dissociation energies of the bonds in the activated complex are similar to the Polanyi–Semenov equation. Hence, the regions of applicability of the two equations should be the same. However, the Polanyi–Semenov equation is applicable only to the reactions of radicals with aliphatic hydrocarbons, in which structurally uniform activated complexes[119] are formed.

V. SEPARATION OF POLAR AND RESONANCE EFFECTS IN FREE-RADICAL REACTIONS

In this Section we shall discuss the application of the two-parameter Taft equation

$$\lg \frac{k_{sub}}{k_0} = \rho^{\cdot}\sigma^{\cdot} + r^{\cdot}\sigma^{r} \qquad (11)$$

to the study of the reactions of free radicals with compounds whose substituents show both polar and resonance effects. Clearly, Eqn. (11) is applicable only if the steric effect of the substituents is negligible.

In contrast to ordinary substitution reactions, whose transition state contains a formally quinquevalent carbon atom (as in the S_N2 reactions, for example), free-radical substitution reactions proceed through a transition state with little steric hindrance:

$$Y^- + CR_1R_2R_3X \rightarrow \left[\begin{array}{c} R_1 \quad R_2 \\ Y \ldots C \ldots X \\ \quad | \\ \quad R_3 \end{array}\right]^- \rightarrow YCR_1R_2R_3 + X^- \quad S_N2 \text{ mechanism}, \qquad (21)$$

$$Y^{\cdot} + CR_1R_2R_3X \rightarrow [Y \ldots X \ldots CR_1R_2R_3] \rightarrow YX + {}^{\cdot}CR_1R_2R_3 \quad \text{Free-radical substitution mechanism}. \qquad (22)$$

§ A new method of calculating the activation energy of free-radical reactions, based on a presentation of the potential energy of the reacting system in terms of Morse curves, has recently been suggested[157,158].

Therefore, the steric effect can often quite correctly be ignored. However, in the presence of several substituents we must consider a special form of the steric effect, in which resonance in the transition state is geometrically precluded. In the following calculations we shall confine ourselves, as a rule, to the rate constants of monosubstituted compounds, with the exception of methyl and halogen substituents.

Only the polar constants (σ^*) of Taft's equation[2] were available in the literature. Therefore, one particular series of free-radical substitution reactions (the reactions of primary alkyl radicals in the liquid phase) was used to calculate the resonance constants σ^r of the substituents by Eqn. (11). As stated above (p. 220), the chain transfer constants $C_{\geqslant 3}$ in the telomerisation of ethylene with halogenomethanes obey the Taft equation in its simplest form (Eqn. (9)), the proportionality constant ρ^* having the value 2.33 to a first approximation irrespectively of the nature of the atom abstracted (H, Cl, or Br). Hence, σ^r was determined from the chain transfer constants $C_{\geqslant 3}$ of monosubstituted derivatives of methane with substituents showing both polar and resonance effects. It was assumed that for this reaction $\rho^* = r^* = 2.33$. This assumption is undoubtedly arbitrary, but it seemed a reasonable one because it yields a single scale for the quantities σ^* and σ^r. However, it must be borne in mind that whereas a change in r^* will produce a change in the absolute value of σ^r, their relative values will remain unchanged. Thus,

$$\sigma^r = \frac{1}{2.33} \lg \frac{C_{sub}}{C_0} - \sigma^*. \qquad (23)$$

The measured chain transfer constants $C_{\geqslant 3}$ for the telomerisation of ethylene with methyl, ethyl, and isopropyl iodide[108,109], 1,1-dichloroethane[89], bromoacetic acid[159], toluene, acetone, acetic acid, and acetonitrile[160] (at 100°) were inserted into Eqn. (23), and also the chain transfer constants for the polymerisation of ethylene with methanol and propylene (at 130° and 1350 atm), obtained by Mortimer[161]. (Although these latter data were obtained at a higher temperature, the effects of temperature and pressure increase can be expected to be mutually compensating to a large extent.)

The results of our calculations are shown in Table 4. The value of $\sigma^r_{CH_2COOH}$ adopted is the average of the values calculated from the chain transfer constants for acetic and bromoacetic acid. The resonance constants of the alkyl substituents were calculated from the chain transfer constants of alkyl iodides. $\sigma^r_{CH_2CH_3}$, found from the chain transfer constant of 1,1-dichloroethane ($C_3 = 0.178$), is practically the same as the value obtained from $C_3^{C_2H_5-I}$.

The resonance effects of the substituents in the substrate molecule which reacts with a free radical are probably determined mainly by the delocalisation of the unpaired electron onto these substituents in the transition state of the reaction. There is nothing new, essentially, in this point of view. The interaction of the unpaired electron with substituents in free radicals has been demonstrated many times. Thus, it has been shown that the stabilisation energy of benzyl radicals is increased by the presence of alkyl substituents[162]. Gilbert and Kreilick[163] have calculated the distribution of the unpaired electron density in substituted phenoxy radicals. They found that the delocalisation of the unpaired electron increases when the substituents $CH_2COOC_2H_5$, $C(CH_3)_3$, and CH_3CO are introduced in the *para*-position.

Furthermore, the distribution of unpaired electron density has a significant effect on the reactivity of the free radical. Thus, the rate of reaction of the methyl radical at the *ortho*-position, the *para*-position, and the oxygen atom of the phenoxy radical depends on the distribution of spin density in the latter radical[164]. Similarly, a relationship has been found between the unpaired electron density distribution in phenoxy and aryloxy radicals and the activation energy of their reactions with t-butyl peroxide[165,166].

Table 4. Resonance constants of the substituents (σ^r) and spin densities in the resulting free radicals (p_R).

R–X	$C_{\geqslant 3}$ (100°)	σ^{*a}	σ^r	p_R
CH_3–I	4.5 [109]	0	0	1.000
CH_3CH_2–I	14.8 [109]	−0.10	0.32	0.919 [167]
$(CH_3)_2CH$–I	48.3 [109]	−0.20	0.64	0.844 [167]
CH_3–H	$1.5 \cdot 10^{-6}$ [a] [86]	0	0	1.000
$HOOCCH_2$–H	0.0037 [160]	1.05	0.40	0.923 [168]
CH_3–Br	0.0025 [a] [159]	0	0	1.000
$HOOCCH_2$–Br	3.7 [159]	1.05	0.31	0.923 [168]
$NCCH_2$–H	0.0283 [160]	1.3	0.54	0.852 [169]
$C_6H_5CH_2$–H	0.0254 [160]	0.215	1.605	0.621[c]
CH_3COCH_2–H	0.0290 [160]	1.12[c]	0.72[c]	0.830 [170, 171]
CH_2=$CHCH_2$–H	0.015[b] [161]	0.1	1.62	0.604 [172]
$HOCH_2$–H	0.0021[b] [161]	0.555	0.795	0.840 [169]
CH_3OCH_2–H		0.520	0.97[c]	0.770 [173]
$C_6H_5OCH_2$–H		0.85	0.66[d]	0.848[c]
CH_3CO–H		1.65	1.15[d]	0.728[c]

a) Calculated value. b) Chain transfer constants in the polymerisation of ethylene at 130° and 1350 atm. c) Obtained by Eqn. (25). d) Obtained from the rate constants for the methyl radical reactions (Table 5) by Eqn. (11).

The delocalisation of the unpaired electron on the substituents of the substrate molecule in the transition state of a free-radical reaction can be compared with the spin-density distribution in the resulting free radical. These ideas were developed by Dixon[174]. However, he points out that direct comparison of spin-density distribution in the radicals with the reactivity of the reacting molecules is impossible, because radicals (unlike molecules) have a planar structure. Therefore, Dixon prefers to use the spin–spin interaction constants of vicinal protons to characterise the delocalisation of electron spin in the transition state. Nevertheless, the transition state for radical substitution reactions involving monosubstituted compounds hardly ever presents geometrical restrictions to the delocalisation of the unpaired electron on the substituent. Hence, we believe that the resonance effect of substituents can be directly related to the spin density in the radicals (calculated from ESR spectra).

We have used spin-density values obtained from the most accurate form of the McConnell equation for the hyperfine structure (HFS) constants of the protons in the methyl groups of the $CH_3\dot{C}HX$ radicals[167,169]:

$$\rho_R = \frac{a^{CH_3}}{29.3\,(1 - 0.081)}. \qquad (24)$$

In this equation, ρ_R is the spin density at the α-carbon atom of the $XCH_2^{\cdot}$ radical, a^{CH_3} is the HFS constant of the freely rotating methyl group of the $CH_3\dot{C}HX$ radical, the factor $(1 - 0.081)$ allows for the delocalisation of the unpaired electron on the CH_3 group[167]. (The traditional

symbol ρ for the spin density has been replaced by p_R to avoid confusion with the proportionality constants ρ and ρ^* of the Hammett–Taft equations.) Values of p_R are listed in Table 4.

We have tried to establish a relationship between the resonance constants σ^r of the substituents, calculated by Taft's Eqn. (11), and the spin density on the substituents in the resulting free radicals, in the form of the equation[175-177]:

$$\sigma^r = b(1 - p_R). \quad (25)$$

Eqn. (25) was solved for the σ^r and p_R values of the radicals $CH_3^\cdot$, $CH_3CH_2^\cdot$, $(CH_3)_2CH^\cdot$, $HOOCCH_2^\cdot$, $NCCH_2^\cdot$, $CH_2{=}CHCH_2^\cdot$, and $HOCH_2^\cdot$. The result, obtained by least squares, was

$$\sigma^r = (4{,}23 \pm 0{,}48)(1 - p_R), \quad \text{correlation coefficient } 0.988. \quad (26)$$

This expression can be used to calculate new values of σ^r and p_R, and other derived quantities. Thus, we obtained $\sigma^r_{CH_2COCH_3} = 0.72$, $\sigma^r_{CH_2OCH_3} = 0.97$, and $\sigma^r_{CH_2C_6H_5} = 0.621$. Since the chain transfer constant for the telomerisation of ethylene with acetone is known ($C^{CH_3COCH_3}_{\geqslant 3} = 0.0290$, Table 4), it follows that $\sigma^r_{CH_2COCH_3}$ can be found in the same way as the other resonance constants: from Eqn. (11) and the known polar constant $\sigma^*_{CH_2COCH_3} = 0.60$.[2] However, this method of calculation gives the anomalously high value $\sigma^r_{CH_2COCH_3} = 1.24$. Therefore, we prefer to use a different value of $\sigma^*_{CH_2COCH_3}$ for free-radical processes. Inserting $\sigma^r_{CH_2COCH_3} = 0.72$ into Eqn. (11) we obtain $\sigma^*_{CH_2COCH_3} = 1.12$. As we shall show below, the new value of $\sigma^*_{CH_2COCH_3}$ can be used with advantage in the study of other free-radical reactions.

The spin-density distribution in the benzyl radical has been determined theoretically by several workers, but the value of $p_{CH_2C_6H_5}$ depends very appreciably on the method of calculation (see, for example, Ref. 178). Inserting into McConnell's Eqn. (24) the value $p_{CH_2C_6H_5} = 0.621$ found by Eqn. (26), we can find a^{CH_3} for the ESR spectrum of the $C_6H_5\dot{C}HCH_3$ radical: $a^{CH_3} = 29.3\ (1 - 0.081)p_{CH_2C_6H_5} = 16.8$ G. It is interesting to note that in a recent paper[179] the HFS constants $a^H = a^{CH_3} = 16.5$ G are proposed for the $C_6H_5\dot{C}HCH_3$ radical.

The Taft equation with polar and resonance terms (Eqn. (11)) can be applied to the reactivity of monosubstituted methane derivatives towards free radicals. All the data available at the time of writing are collected in Tables 5 and 6. We have included only those radicals for which more than four rate constants were known. This gave at least four equations to be solved for evaluating the results by least squares. Since the chain transfer constants of polymeric radicals are the least accurately known, only the constants obtained in the polymerisation of vinyl acetate were considered, because this reaction has been fully characterised. As the Table shows, three correlations were obtained for five reaction rate constants involving the radicals $CH_3(CH_2)_2\dot{C}H(CH_2)_2CH_3$, $HO^\cdot$, $Na^\cdot$: one for six values ($I^\cdot$), one for eight values ($CH_3^\cdot$), one for nine values (polyvinyl acetate radical), and two for ten values ($CF_3^\cdot$ and $C_6H_5^\cdot$).

Table 5. Application of Taft's Eqn. (11) to the rate constants of reactions between free radicals and R–H compounds.

R–H	Rate constants in the gas phase (g.p.) and liquid phase (l.p.)							
	$X(CH_2CH_2)_n^\cdot$ $C^a_{\geqslant 3}$ l.p. 100°	$CH_3^\cdot$ $k\cdot10^{-6}$, g.p. 100° $cm^3\ mole^{-1}\ s^{-1}$	$CH_3(CH_2)_2\dot{C}H(CH_2)_2CH_3$ $C^3_{\geqslant 3}$ l.p. 100°	$CF_3^\cdot$ $k\cdot10^{-6}$, g.p. 100° $cm^3\ mole^{-1}\ s^{-1}$	$\frac{k}{k_{CCl_4}}$ $C_6H_5^\cdot$ l.p. 60°	$HO^\cdot$ [b] $k\cdot10^{-11}$ l.p. $cm^3\ mole^{-1}\ s^{-1}$ 20°	$I^\cdot$ $k\cdot10^{-4}$ g.p. $cm^3\ mole^{-1}\ s^{-1}$	$X(CH_2\dot{C}H)_n$ | $OCOCH_3$ $C^a\cdot10^4$ l.p. 60°
CH_3–H	[c]	0.0019 [180]	$3.9\cdot10^{-6}$ [h, i]	0.36 [d 198–200]	0.005 [h, i]	0.07 [h, i]	0.0025 [217]	[k]
$ClCH_2$–H				0.83 [200]	0.07 [14]			
Cl_2CH–H			0.25 [196]	5.54 [201]	0.48 [14]			4 [221]
Cl_3C–H			9.6 [196]	17.7 [d 199, 201]	3.2 [14]	0.074 [211]		140 [221–223]
$BrCH_2$–H				0.70 [200]				
$HOCH_2$–H		0.23 [d 181, 1 2]		18.6 [202, 203]	0.13 [14]	5.36 [d 212–215]	0.40 [218]	6 [221]
$HOOCCH_2$–H		0.15 [e 183]			0.086 [14]	0.166 [212, 215]		10 [221]
$NCCH_2$–H		0.90 [184]						10 [221]
CH_3COCH_2–H		0.65 [d 180, 185 c, 187]	0.125 [197]	5.47 [204]	0.17 [14]	0.64 [d 211, 212, 215]		19 [d 222, 224]
CH_3OCH_2–H		0.62 [d, g 182, 185, 189]		52.5 [205]	0.28 [14]		5.8 [218]	
CH_3CO–H		33.1 [g 190]		243 [206]	2.4 [208]	5.13 [j]	520 [218]	420 [d 221, 223–225]
$C_6H_5OCH_2$–H		0.35 [g 191]	0.14 [197]		0.07 [20]			10 [196]
$CH_2{=}CHCH_2$–H		1.33 [d 185, 192]					56 [219]	
$C_6H_5CH_2$–H		1.16 [d 185, 188, 193–195]	1.24 [197]	135 [207]	0.33 [d 17, 210]		25 [220]	25 [d 221, 222, 224, 226]
ρ^*	2.33	1.51±0.14	2.70±0.53	0.56±0.14	1.11±0.07	0.01±0.20	1.67±0.32	1.02±0.16
r^*	2.33	1.51±0.14	2.22±0.26	1.55±0.05	0.90±0.13	1.62±0.34	3.13±0.24	1.21±0.12
r			0.962	0.994	0.936	0.959	0.952	0.968

a) Chain transfer constants. b) Rate constants for the reactions of $HO^\cdot$ at pH 7 were chosen for the calculation, because hydroxyl radicals are converted into $O^\cdot$ in alkaline media[231]. c) These values of chain transfer constant were used to calculate σ^r (see Table 4). d) Mean value. e) Reaction with CH_3COOCD_3. f) All these rate constants were recalculated using a corrected value[186] for the rate constant of the recombination of methyl radicals (2.3×10^{13} $cm^3\ mole^{-1}\ s^{-1}$). g) The rate constants for the reactions of methyl radicals were used to calculate the corresponding σ^r. h) Calculated from Taft's Eqn. (11). i) Chloroform taken as standard compound. j) Obtained from $k_{CH_3CHO}/k_{CH_3OH} = 2.25$[216] and $k_{CH_3OH} = 5.36\times10^{11}$ $cm^3\ mole^{-1}\ s^{-1}$. k) Toluene taken as standard compound in Eqn. (11).

All the available data (except a few doubtful ones) were used to analyse the rate constants of the gas-phase reactions of the methyl radical. For example, the results of Raal and Steacie for the reactions of $CH_3^{\cdot}$ with halogenomethanes were not included, because hydrogen halides are formed in these reactions[227-229]. As Table 5 shows, the rate constants for the reactions of methyl radicals are fitted by Eqn. (11) for the special case of $\rho^* = r^* = 1.51 \pm 0.14$. This is not unexpected, since the constant r^* had been taken to be equal to ρ^* for the reactions of alkyl radicals in the liquid phase. Calculations by Eqn. (11) with $\rho^* \neq r^*$ confirmed that these quantities cannot differ by more than 0.17 of a unit of ρ^* for the reactions of methyl radicals. From this correlation expression, and the known rate constants for the reactions of the methyl radical with anisole[191] and acetaldehyde[190], we obtain $\sigma^r_{CH_2OC_6H_5} = 0.66$ and $\sigma^r_{COCH_3} = 1.15$, and also $p_{CH_2OC_6H_5} = 0.848$¶ and $p_{COCH_3} = 0.728$. These resonance constants have been used to set up correlation expressions for other free radicals.

Table 6. Application of Taft's Eqn. (11) to the rate constants of the reactions of sodium atoms with R–Cl compounds.

Rate constant	$(CH_3)_3CCl$	$(CH_3)_2CCl_2$	CH_3CCl_3	CCl_4	$CH_2=CHCH_2Cl$	ρ^*	r^*	r
$k \cdot 10^{-11}$ (Ref. 232) cm^3 mole^{-1} s^{-1} at 247°, g.p.	2.76	42.3	393	2260	27.3	1.234 ±0.007	0.760 ±0.016	0.9996

The correlation expressions for the reactions of other free radicals were obtained in a similar way. The rate constant for the reaction of the phenyl radical with acetonitrile[14] was not included in the calculation because it showed a serious discrepancy, probably associated with the experimental errors inherent in the chosen method[17] of measurement of k. In the study of the reactions of the hydroxyl radical in aqueous solutions the rate constants of the reactions with methane and acetonitrile[214] were excluded from the calculation because the measurements had been made at pH 9, i.e. under conditions where the radical anion $O^{\cdot-}$ is also present[231].

It is evident from Tables 5 and 6 that our correlation expressions have an accuracy of 10–25% for ρ^* and 10–15% for r^*. The only exception is the value of ρ^* for the reactions of the trifluoromethyl radical, which lies within the range from –0.20 to +0.20. These errors are fairly large, but all the correlation coefficients (except for one value of 0.936 for the reactions of the phenyl radical) are greater than 0.950, and two of them are greater than 0.990. Thus, we may conclude that the correlation is entirely satisfactory†.

We must stress that these calculations were made with data from different sources and having different precision. Furthermore, the rate constants of free-radical reactions can seldom be measured to an accuracy of better than 50%. Also, the number of available data was so small that it was not always possible to exclude values of doubtful reliability from the calculation. Hence, the correlation errors are relatively large at this stage, but we think it likely that the correlation will improve when a larger fund of accurate experimental data becomes available.

A qualitative dependence of ρ^* on the electronegativity of the free radicals can be observed for reactions of a given type (ignoring temperature differences and different reaction media). It is found that ρ^* decreases in the sequence

$$X(CH_2CH_2)_n^{\cdot},\ CH_3(CH_2)_2\dot{C}H(CH_2)_3CH_3 > CH_3^{\cdot},\ I^{\cdot} > C_6H_5^{\cdot} > CF_3^{\cdot} > HO^{\cdot}.$$

In this series the electronegativity of the radicals increases from left to right. The value of r^* should be independent of the polar properties of the radicals, and should be determined only by the structure of the transition state of the reaction. The dependence of r^* on the structure of the transition state is discussed again below.

The effect of the statistical factor has been ignored in all the above calculations. "Intuitively", the statistical factor should be equal to the number of equally probable centres of attack of the reagent (for example, the free radical) on the substrate molecule. Benson[234] has tried to develop the concept of a statistical factor from the theory of absolute reaction rates. He has shown that it is not obvious, in general, that the "intuitive" statistical factor can be identified with a factor giving the symmetry numbers in the theoretical rate constant equation. Studies of reactions involving the hydrogen atom[235,236] have shown that the real statistical factor, calculated from the ratio of the pre-exponential terms in the rate constants for the reactions, is not the same as the factor given by "intuitive" considerations. It should be noted that a one-sided calculation of the statistical factor is objectionable also from general considerations, since other, "non-chemical" contributions to the rate constant must be taken into account (for example, the effect of moments of inertia[236]).

¶ Hudson and Root[230] have recently obtained the value $p_{CH_2OCH_3} = 0.831$ by using Eqn. (24) in conjunction with ESR data.

† Migita and coworkers[233] conclude, by comparing the rate constants for the chlorination of chloroalkanes and chlorosilanes, that the resonance effect of chlorine atoms in the α-position to the reaction centre is greater than the hyperconjugation effect of the C–H and C–C bonds. We observe that these workers' rate constants for the chlorination of chloroalkanes and nitriles[92-94,233], obey Taft's Eqn. (11) with $\rho^* = -3.54 \pm 0.28$ and $r^* = 1.27 \pm 0.40$ (at 40°) except for compounds with chlorine atoms in the α-position to the reaction centre. If the rate constants for the chlorination of chloroalkanes with chlorine atoms in the α-position are inserted into this equation, the accelerating effect of chlorine as an α-substituent is found to correspond to $\sigma^r_{CH_2Cl} = 1.5$ and $\sigma^r_{CH_2Cl} = 3.2$. (We note that σ^r for a classical resonance-inducing substituent such as $-CH_2CH{=}CH_2$ is 1.62 (Table 4)). Therefore, we suggest that the effect of chlorine atoms as α-substituents on the rate of chlorination of chloroalkanes should be ascribed not to the resonance effect of chlorine, but to some other effect (for example, the change in hybridisation of the carbon atom).

Nevertheless, all the correlation expressions obtained (as well as some published data[98]) were recalculated to allow for the statistical factor: the effect on the results was negligible within the quoted error limits. In four cases the correlation was more satisfactory without the statistical factor, in four cases the correlation was improved by the statistical factor, and in one case the statistical factor had no effect. None of the effects was large.

Steric preclusion of resonance

As already pointed out (p. 224), the presence in the substrate molecule of several substituents exhibiting a resonance effect can lead to a spatial disturbance of the conjugation of the unpaired electron with the substituents in the transition state of the reaction. Steric preclusion of the resonance was observed in a number of systems, for example in studies of the addition of a methyl radical to unsaturated and to aromatic compounds.[146]

In our calculations of the resonance constants of the ethyl and the isopropyl radical from the chain transfer constants of these radicals in the telomerisation of ethylene with alkyl iodides we found (Table 4) that the resonance effect of two methyl groups is equal to twice the effect of a single methyl group ($\sigma^r_{CH(CH_3)_2} = 0.64$, $\sigma^r_{CH_2CH_3} = 0.32$). This was confirmed by measuring the chain transfer constants in the telomerisation of ethylene with ethyl bromide and isopropyl, and also by inserting the σ^r values obtained into the correlation equations. Hence, no steric preclusion of resonance occurs in radical substitution reactions when a second methyl group is introduced into the substrate molecule.

However, a study by the competitive method of the reactivity of the compounds $CH_3COOH - ClCH_2COOH - CH(COOH)_2$ and $BrCH_2COOH - BrClCHCOOC_2H_5 - BrCH(COOC_2H_5)_2$ has shown that the introduction of chlorine or a second carboxyl into a molecule of acetic or bromoacetic acid increases the chain transfer constant by a factor of 35–25 and 14–4 respectively[159,177]. Using Taft's equation it is readily shown that the reactivity of these compounds can be expressed as the overall effect of the CHClCOOR group (with R = H or C_2H_5), $\Sigma\sigma^* = 1.86-2.10$, and of the group $CH(COOR)_2$, $\Sigma\sigma^* = 1.64-2.06$. (By analogy with other reactions of n-alkyl radicals the proportionality constant is taken to be $\rho^* = 2.33$). Although the polar constants σ^* of these groups are unknown, we can establish that the observed overall effects of the CHClCOOR and $CH(COOR)_2$ groups are almost fully accounted for by the polar effect, noting that $\sigma^*_{CH_2COOH} = 1.05$ [2] and allowing for the "saturation effect" in the summation of the inductive constants (for example, $\sigma^*_{CH_2Cl} = 1.05$, $\sigma^*_{CHCl_2} = 1.94$, $\sigma^*_{CCl_3} = 2.65$). Thus, in these cases the preclusion of resonance is almost total.

VI. RELATIONSHIP BETWEEN THE TRANSITION-STATE STRUCTURE AND THE REACTIVITY OF FREE RADICALS

In the applications of Taft's two-parameter Eqn. (11) to studies of the reactions of alkyl radicals with alkyl bromides and iodides[109,159], and also of the reactions of sodium atoms with alkyl chlorides (Table 6), methyl groups were examined among other substituents. It was found that the effect of methyl groups, like that of the other substituents, can be resolved into a polar and a resonance component. However, in the more general case the influence of alkyl groups in free-radical reactions cannot be described in terms of these two effects alone.

Deviations from Eqn. (11) in the case of methyl substituents are observed in the reactions of free radicals with aliphatic hydrocarbons. The effect of methyl groups on the rate of hydrogen abstraction by radicals from methane, ethane, and propane could have been expected to be additive, as is found for example in the reactions of radicals with methyl-, ethyl-, and isopropyl halides with C–X bond breaking[109,159]. However, as Table 7 shows, the increase in reaction rate for all radicals is much greater on going from methane to ethane than from ethane to propane. Thus, the Taft equation (Eqn. (11)) cannot be applied to these reactions, since the quantities ρ^* and r^* are a function of R′ in the reactions

$$R^{\cdot} + H{-}R' \rightarrow RH + R'^{\cdot} \quad [R' = CH_3, CH_2CH_3, CH(CH_3)_2]. \qquad (27)$$

The writer has shown[237] that a direct proportionality exists between $\lg(k_{C_2H_6}/k_{CH_4})$ (see Table 7) and the dissociation energy of the R–H bond formed in reactions (27). By least squares, the following relationship was obtained

$$\lg\frac{k_{C_2H_6}}{k_{CH_4}} = -(0.048\pm0.005)D(R{-}H) + (6.62\pm0.50), \quad r = 0.913. \qquad (28)$$

As stated above (p. 222), the proportionality coefficient α of Polanyi's Eqn. (17) depends on the structure of the transition state for the reaction. If the ratio of the pre-exponential factors for the reactions with ethane and methane is independent (to a first approximation) of the nature of the attacking free radical, the dependence of α on $D(R-H)$ can easily be obtained from Eqn. (17). Thus, for the reactions with methane and ethane, we have

$$\alpha = \frac{E_{ac}^{CH_4} - E_{ac}^{C_2H_6}}{D(CH_3-H) - D(C_2H_5-H)}, \qquad (29)$$

$$\alpha = \frac{2.3RT}{6000}\lg\frac{k_{C_2H_6}}{k_{CH_4}} - \frac{2.3RT}{6000}\lg\frac{A_{C_2H_6}}{A_{CH_4}}, \qquad (30)$$

where $D(CH_3-H) = 104$ kcal mole^{-1}, $D(C_2H_5-H) = 98$ kcal mole^{-1}.[210] For $\lg(A_{C_2H_6}/A_{CH_4}) = \text{const} \simeq 0$, and $T = 373°K$, we have from Eqns. (28) and (30)

$$\alpha = \frac{2.3RT}{6000}[-(0.048\pm0.005)D(R{-}H) + (6.62\pm0.50)] =$$
$$= -(0.014\pm0.001)D(R{-}H) + (1.89\pm0.14) \qquad (31)$$

These ideas were tested by calculating α directly from formula (29), using published activation energies for the reactions of the radicals F$^{\cdot}$, Cl$^{\cdot}$, Br$^{\cdot}$, I$^{\cdot}$, ROO$^{\cdot}$, $CD_3^{\cdot}$, $CF_3^{\cdot}$, O$^{\cdot}$, H$^{\cdot}$, HO$^{\cdot}$. (The activation energies, as a rule, are known less accurately than the rate constants for the reactions. Hence, the values for the radicals $C_2F_5^{\cdot}$, n-$C_3F_7^{\cdot}$, and CN$^{\cdot}$, which were found to give an unsatisfactory correlation, were ignored). The result was

$$\alpha = -0.015D(R{-}H) + 2.03.$$

It is clear that the agreement with Eqn. (31) is excellent. The values $\alpha_{CH_3} = 0.44$ and $\alpha_{Br} = 0.66$ may be compared with those reported by Trotman-Dickenson (0.49 [127] and 0.86 [129] respectively).

Eqn. (31) is a quantitative statement of Hammond's postulate[10], since α varies from 0 to 1 on going from the initial to the final state[119]. Thus, in accordance with the postulate, the transition state for the most active radical (F$^{\cdot}$) is indistinguishable from the initial state, i.e. $\alpha = 0$,

Table 7. Kinetic parameters of the reactions of free radicals (R·) with methane, ethane, and propane, and dissociation energies of the bonds (D(R–H)).

Radical R·	k_{CH_4}	$k_{C_2H_6}$	$k_{C_3H_8}$	$\lg \frac{k_{C_2H_6}}{k_{CH_4}}$	$E_{CH_4} - E_{C_2H_6}$, kcal mole^{-1} [a]	α	D(R–H) kcal mole^{-1}
	cm^3 mole^{-1} s^{-1}						
CH_3·	$1.9 \cdot 10^8$ [180]	$7.0 \cdot 10^{4}$ [b, c 238, 239]	$8.0 \cdot 10^5$ [241]	1.57	3.15	0.44	104 [242]
CF_3·	$3.6 \cdot 10^5$ [b 198—200]	$17.6 \cdot 10^6$ [b 198, 243]	$7.6 \cdot 10^7$ [211]	1.69	2.0	0.40	106.3 [244]
C_2F_5·	$2.7 \cdot 10^5$ [245]	$12.2 \cdot 10^6$ [245]		1.655	1.9?	0.45	103 [244]
n-C_3F_7·	$2.7 \cdot 10^5$ [246]	$7.3 \cdot 10^6$ [246]		1.43	0.3?	0.45	103 [244]
H·	$1.38 \cdot 10^7$ [247]	$40.5 \cdot 10^7$ [248]	$2.1 \cdot 10^9$ [235]	1.47	2.6	0.43	104.2 [249]
HO·	$5.9 \cdot 10^{10}$ [250]	$10 \cdot 10^{11}$ [250]		1.23	1.4	0.22	119.2 [249]
ROO·	3.16 [251]	646 [251]	$3.7 \cdot 10^4$ [251]	2.31	4.0	0.63	90.0 [252]
O	$8.51 \cdot 10^7$ [253]	$4.85 \cdot 10^8$ [253]		1.755	3.1	0.46	102.3 [249]
F·	$1.9 \cdot 10^{13}$ [254]	$3.3 \cdot 10^{13}$ [254]	$1.1 \cdot 10^{13}$ [254]	0.24	0.93	0.0	135.5 [249]
Cl·	$4.0 \cdot 10^{11}$ [b 255, 256]	$24 \cdot 10^{12}$ [b 255, 256]	$29 \cdot 10$ [b 255, 256]	1.78	2.9	0.45	103.1 [249]
Br·	$1.4 \cdot 10^9$ [b 257—259]	$1.2 \cdot 10^6$ [b 258, 260]	$5.8 \cdot 10^7$ [258]	2.92	5.1	0.66	87.6 [249]
I·	$6.3 \cdot 10^{-6}$ [217]	$7.9 \cdot 10^{-3}$ [261]	0.43 [262]	3.11	6.2	0.89	71.3 [249]
CN	1	7.1 [d 263]	7.0 [d 263]	0.85	3.7?	0.34	111 [249]

a) Difference in activation energies; literature references are given in the previous columns. b) Mean value. c) Value of $k_{C_2H_6}$ calculated by using a corrected value of the rate constant for the reaction of the methyl radical with deuteroacetone [240]. d) Rate constants relative to the value for methane, taken as unity.

whereas for I· we have $\alpha = 0.89$, i.e. the transition state adopts the structure of the products almost completely. It follows that Eqns. (28) and (31) are correct only for the chosen range of D(R–H) values, since this range corresponds to a change of the transition state structure from the structure of the reactants to that of the products. In particular, when D(R–H) = 0, $\lg(k_{C_2H_6}/k_{CH_4}) \neq 6.62$ (the value required by Eqn. (28)).

In the reactions of $CH_3^{\cdot}$, $CF_3^{\cdot}$, Cl·, $C_2F_5^{\cdot}$, n-$C_3F_7^{\cdot}$, H·, and O· the transition state is "symmetrical" as expected, i.e. it is mid-way between the initial and the final configuration, since the dissociation energies of the bonds broken and formed in the reactions with methane are approximately equal for these radicals. Published data on the structure of the transition state for the reactions between methyl radicals and hydrocarbons support this conclusion (~50% of initial state character [185]), but earlier work [264] on the transition state of reactions with chlorine had detected only 10% of final state character in the transition state instead of 50% as found in our work. These results were obtained by comparing the differences in activation energy for the removal of primary and tertiary hydrogen atoms in triptane by chlorine atoms with the dissociation energies of these bonds.

However, the absolute rate constants for the reactions of chlorine with ethane, propane, and isobutane are approximately equal: $(2-3) \times 10^{13}$ cm^3 mole^{-1} s^{-1} at 100°. [255,256] Hence, the small difference in activation energy of these reactions is explained by the fact that practically every collision between the reactants leads to reaction—the upper limit of the rate constant for bimolecular reactions is given as 10^{14} cm^3 mole^{-1} s^{-1} by the collision theory—and changes in the structure of the alkane molecule have practically no effect on the reaction rate. However, on going from methane to ethane the rate of reaction of chlorine atoms increases approximately 60-fold (at 100°), and the activation energy changes by 2.9 kcal mole^{-1}, i.e. the reaction rate is very sensitive to the structure of the alkane. Hence, it is more correct to use these data to calculate the structure of the transition state.

It is interesting to note that the transition state has the same structure (~50% of initial state character) for a large number of radicals. This explains why the Polanyi–Semenov equation is so generally applicable.

From the above we may conclude that the increase in the rate constants of free-radical reactions on going from methane to ethane is due first of all to the decrease (by 6 kcal mole^{-1}) in the dissociation energy of the bond to be broken. Bond dissociation energies are also the rate determining factor in the reactions of other alkanes with free radicals. For each radical, the transition-state structure is the same in all the reactions, since Eqn. (17) applies. In the radical reactions of compounds whose substituents have strong polar and resonance effects (chloroform, toluene, etc.) the transition-state structure may differ from that of the same reactions with alkanes. Thus, the points for the reactions of the methyl radical with toluene and propylene [119] fall well away from the plot of Eqn. (17).

Eqns. (28) and (30) can be used either to calculate the kinetic parameters of free-radical reactions or to predict bond energy values (D(R–H)) and the parameter α. Thus, Pritchard and Perona [265] recently measured the rate constants of reactions (27) with the radical $CHF_2^{\cdot}$. They found $\lg(k_{C_2H_6}/k_{CH_4}) = 2.02$ at 100°. From Eqns. (28) and (31) we obtain $D(CHF_2\text{–H}) = 95.9$ kcal mole^{-1}, $\alpha = 0.55$. The experimental value of $D(CHF_2\text{–H})$ is 97.4 kcal mole^{-1}.

As was stated above (p. 226), the proportionality constant r^* of Eqn. (11) should depend on the structure of the transition state and therefore also on the parameter α. Unfortunately, the r^* values given in Table 5 refer to different temperatures, which makes it hard to compare them. However, there can be little doubt that r^* increases with α. (For example, $r^*_{I^{\cdot}} > r^*_{X(CH_2CH_2)^{\cdot}_n} > r^*_{CH_3^{\cdot}} = r^*_{CF_3^{\cdot}}$; the corresponding values of α from Eqn. (31) are 0.86, 0.52, 0.44, 0.40).

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Progress in the Chemistry of Nitroxyl Radicals

E.G.Rozantsev and V.D.Sholle

Methods of obtaining nitroxyl radicals by the dehydrogenation of hydroxylamines, oxidation of amines, reduction of nitro- and nitroso-compounds and radical addition to nitrones are considered. Problems of the stability of nitroxyl radicals and their reactivity are discussed—redox reactions, radical reactions, complex formation, and reaction without use of the unpaired electron. There is a bibliography of 283 references.

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I. INTRODUCTION

Nitroxyl radicals are compounds which contain the >N–O group with one unpaired electron. The structure of this fragment can be represented as the superposition of two valence structures:

$$>\dot{N}^{+}\!-\!O^{-} \longleftrightarrow >\ddot{N}\!-\!\dot{O}\cdot\cdot$$

Depending on the effects of conjugation and the polarity of the medium the contribution of the first or second boundary structure to the principal state of the radical can be different.

There have been many studies, theoretical and experimental, to find the electronic structure of the nitroxyl radical. Unfortunately, the various results do not agree satisfactorily. Thus, some investigators[1-3] give values of ~ 0.8–0.9 for the spin density on the nitrogen atom ρ_{π}^{N} for non-aromatic radicals (0.6 for aromatic), whereas others[4-6] give $\rho_{\pi}^{N} = 0.3–0.4$.

Wieland referred to aromatic nitroxyl radicals as nitroxide or azoxyl radicals. In several studies this terminology was later extended to hetero-chain and heterocylic radicals which were non-aromatic in behaviour. Generally speaking, the term "nitroxide", and also "aminoxide" is unfortunate since it does not reflect the radical nature of these species and contradicts the rules of official nomenclature of organic compounds. In the Soviet literature the term "iminoksily" (iminoxyls) is used for non-aromatic nitroxyl radicals.

II. METHODS OF OBTAINING NITROXYL RADICALS

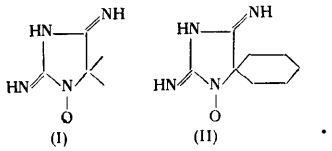
1. Dehydrogenation of Hydroxylamines

The O–H bond of hydroxylamines undergoes homolysis under the action of various reagents and nitroxyl radicals are formed.

In 1901 Piloty and Schwerin[7] obtained the first organic nitroxyl†, porphyrexide (I), by the action of potassium hexacyanoferrate(III) on 1-hydroxy-2,4-di-imino-5,5-dimethylhydantoin; the structure and free radical nature of (I) was established later[9].

† Fremy had obtained the first inorganic nitroxyl ion in 1845 by the oxidation of potassium hydroxylammonium disulphonate with lead(IV) oxide[8].

A spirocyclohexyl analogue of porphyrexide (II) was obtained by the same method in 1944[10]:



(I) (II)

In 1914–1922 Wieland developed a general method for making aromatic nitroxyls which is still widely used. The first stage was the preparation of diarylhydroxylamines:

$$ArNO + XMgAr' \rightarrow Ar\!-\!\underset{\underset{OMgX}{|}}{N}\!-\!Ar' \rightarrow Ar\!-\!\underset{\underset{OH}{|}}{N}\!-\!Ar'$$

The second stage was the single-electron oxidation of the hydroxylamine to a nitroxyl:

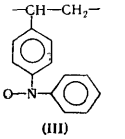
$$Ar\!-\!\underset{\underset{OH}{|}}{N}\!-\!Ar' \xrightarrow{-H'} Ar\!-\!\underset{\underset{O}{|}}{N}\!-\!Ar'$$

Wieland used Ag_2O as the oxidant in the second stage. Diphenyl-, phenyl-*p*-tolyl-, and di-*p*-tolyl-nitroxyls were obtained by this method[11-13]. The first stage of the method can be regarded as a general procedure for obtaining diaryl-, arylalkyl-, and dialkyl-hydroxylamines. In studying the mechanism of this reaction, Murayama showed that the best yields of hydroxylamines are obtained when a large excess of a Grignard reagent is used[14].

Using the Wieland method, Hückel and Liegel[15] obtained phenyl-9-*trans*-decalylnitroxyl in good yield by the action of phenylmagnesium bromide on 9-nitrosodecalin with subsequent oxidation of the hydroxylamine by air.

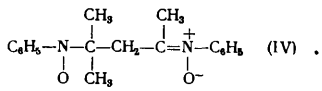
Deguchi and coworkers[16] obtained a series of methyl derivatives of diphenylnitroxyl by the same method.

The macromolecular polyradical (III) was obtained by the reaction of *p*-nitrosopolystyrene with phenylmagnesium bromide followed by oxidation of the hydroxylamine with silver oxide[17]:



(III)

The so-called Kenyon–Benfield radical (IV) is formed in good yield when the condensation product of acetone and phenylhydroxylamine is oxidised[18]‡:

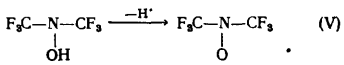


(IV)

Subsequently a series of derivatives of this radical were obtained[19].

Forrester[20] obtained a series of aryl-t-butylnitroxyls by the reaction of ArMgX with t-nitrosobutane and investigated their decomposition products. t-Butylferrocenylnitroxyl was obtained[21] by the action of t-nitrosobutane on ferrocenylmagnesium bromide followed by autoxidation of the hydroxylamine which is formed.

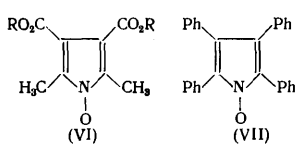
In 1965 Soviet[22,23] and American[24] investigators described the preparation of bis(trifluoromethyl)nitroxyl (V) by the oxidation of the corresponding hydroxylamine:



(V)

The oxidants used were $KMnO_4$, Ag_2O, F_2, and HgO.

In 1963 Rozantsev and coworkers[25] showed that oxidation of certain heterocyclic hydroxylamines of the pyrrol series leads to the formation in the solution of the corresponding nitroxyls (VI):



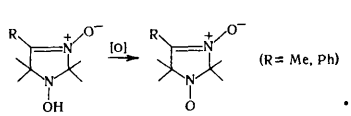
(VI) (VII)

A nitroxyl of similar structure (VII) was isolated by Rio and coworkers[26] in 1968 from the products of the oxidation of 1-hydroxytetraphenylpyrrol by PbO_2.

The same oxidant was used for obtaining acylalkyl-, acylaryl-[27], and arylaminocarbonylarylnitroxyls which are stable in solution[28]. In 1965 Aurich[29] obtained acylphenylnitroxyls by oxidation of the corresponding *N*-hydroxyamides with nickel peroxide[29].

Short-lived aliphatic nitroxyls can be obtained both by the oxidation of hydroxylamines[30,31] and also by photolysis of the latter[31,32].

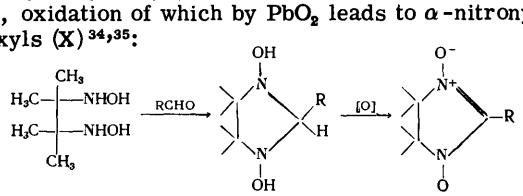
In 1968 Volodarskii and coworkers[33] obtained nitroxyls of structure (VIII) by the oxidation of 1-hydroxy-2,2,5,5-tetramethyl-4-R-3-hydroxyimidazoline by Tollen's reagent or hydrogen peroxide:



(R = Me, Ph)

(VIII)

In the same year Ullman condensed 2,3-bis(hydroxylamino)-2,3-dimethylbutane with aldehydes and obtained 1,3-dihydroxy-4,4,5,5-tetramethyl-2-R-tetrahydroimidazole, oxidation of which by PbO_2 leads to α-nitronylnitroxyls (X)[34,35]:



(IX) (X)

‡ Note added in proof. A cyclic structure has been suggested[283] for (IV).

where R = H, CH_3, C_2H_5, $[CH_2]_{12}CH_3$, CH_2OH, $CH(CH_3)_2$, $CH(OC_2H_5)_2$, C_6H_5, *p*-HOC_6H_4, or *p*-$NO_2C_6H_4$.

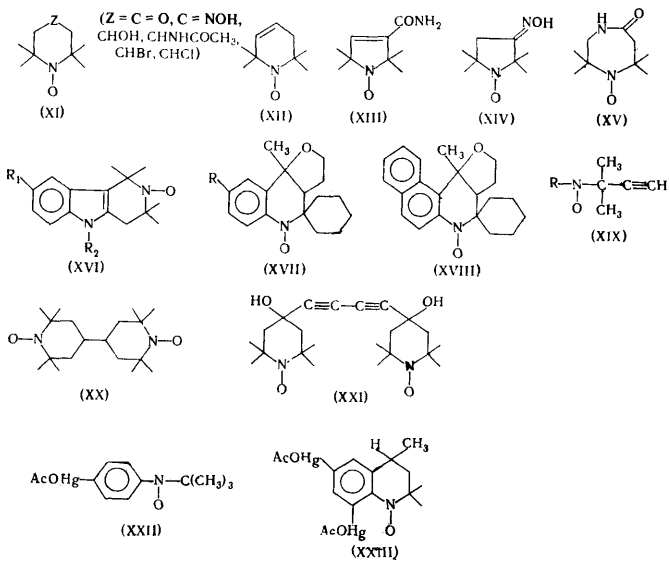
When R = alkyl, the corresponding imidazole can be smoothly oxidised by potassium periodate.

2. Oxidation of Amines

Despite the fact that the preparation of nitroxyls by the oxidation of amines was developed later than the method of dehydrogenation of hydroxyamines, it is now the most important method of making nitroxyls (especially cyclic dialkylnitroxyls).

In 1956 Hoskins[36] recorded the EPR signal of diphenylnitroxyl on passing oxygen into a solution of diphenylamine. Subsequently a large number of nitroxyls was obtained in solution by the oxidation of the corresponding aromatic, aliphatic–aromatic, aliphatic, and acyclic amines. The oxidants used were: hydroperoxides[37–39], hydrogen peroxide with cerium salts[40], RO_2 radicals[41–43], Ag_2O,[44] an alkaline solution of hydrogen peroxide[45], PbO_2,[46] various per-acids[47], the pertungstate ion[48], and benzoyl peroxide[49]. These oxidants can be useful in studying reaction mechanisms and in finding the structure of the nitroxyls.

Oxidation of secondary amines with hydrogen peroxide in the presence of salts of tungstic acid is a convenient method for the preparation of nitroxyls. By this method, developed in our laboratories, stable nitroxyls of the piperidine series (XI) and (XII)[50–53], of hydrogenated pyrrole (XIII) and (XIV)[54,55], of homopiperidine (XV)[56], of carboline (XVI)[57,58], of hydrogenated quinoline (XVII)[59,60], of hydrogenated benzoquinoline (XVIII)[61], aliphatic nitroxyls (XIX)[62], the first non-conjugated biradical (XX)[63], the biradical (XXI)[64], and radicals stable in solution of the benzoxazine, indoline, and carbazole series[65], and organomercury nitroxyls (XXII) and (XXIII)[66] were obtained.



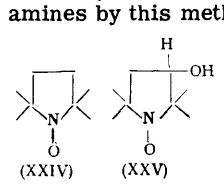
(XI) (XII) (XIII) (XIV) (XV)

(XVI) (XVII) (XVIII) (XIX)

(XX) (XXI)

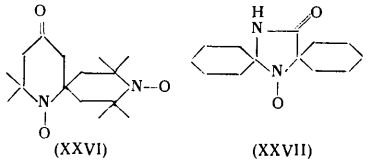
(XXII) (XXIII)

Rassat and coworkers obtained t-butylphenylnitroxyl[67] and certain nitroxyls of the pyrrolidine series (XXIV) and (XXV)[68] on oxidising amines by this method:



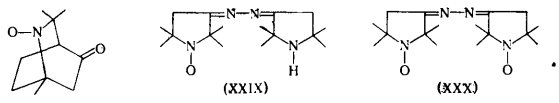
(XXIV) (XXV)

Murayama[69] used the same method to obtain the biradical (XXVI). Then by oxidising 3-oxo-2,5-bicyclohexylimidazoline with hydrogen peroxide in the presence of sodium tungstate in acetic acid medium he obtained the nitroxyl (XXVII)[70].



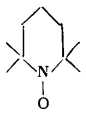
(XXVI) (XXVII)

Oxidation of amines with hydrogen peroxide is readily effected when tungstophosphoric acid and ammonium molybdate are used as catalyst[71]. The monoradicals (XXVIII)[72] and (XXIX)[73] and the biradical (XXX)[73] were obtained by this means. Despite the fact that the use of tungstophosphoric acid accelerates the oxidation the yields of nitroxyls are reduced:



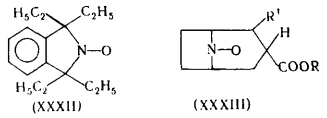
(XXVIII) (XXIX) (XXX)

The mechanism of oxidation of the secondary amines was studied by Lebedev and Kazarnovskii[74], who showed that the oxidant in this instance is the pertungstate ion. They obtained the stable heterocyclic nitroxyl (XXXI):



(XXXI)

Subsequently the method of oxidising amines with hydrogen peroxide in the presence of Na_2WO_4 was extended to tertiary amines. In this way nitroxyls of the isoindoline series (XXXII)[75] were isolated and radicals of the alkaloids of the tropane series (XXXIII) were studied in solution[76]:



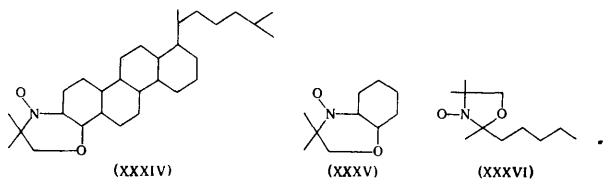
(XXXII) (XXXIII)

In 1964 Tokumaru and coworkers[77] obtained diphenyl, di(methoxyphenyl)-, and di(chlorophenyl)nitroxyls by the action of perbenzoic acid on diarylamines. Di(nitrophenyl)- and dimethoxycarbonyl diphenylnitroxyls are obtained in this instance in very low yields.

Maender and Janzen[78] obtained a large number of triphenylmethyl(alkyl)nitroxyls by oxidation of the corresponding secondary amines with *p*-nitroperbenzoic acid.

Ozone[79], benzoyl peroxide[80], and t-butyl hydroperoxide[81] were used as oxidants in the preparation of nitroxyls from secondary amines.

A specific method for the conversion of ketones into stable nitroxyls has been suggested[82]. On reaction with 2-methyl-2-aminopropanol in the presence of *p*-toluenesulphonic acid, ketones give oxazolidines, which are oxidised by *p*-chloroperbenzoic acid to form the corresponding nitroxyls. The nitroxyls (XXXIV)–(XXXVI) were obtained by this method:

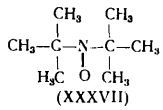


(XXXIV) (XXXV) (XXXVI)

This method was convenient for obtaining certain "spin-labelled" analogues of lipids[83] and steroids[84].

3. Reduction of Nitro-compounds

On reducing $(CH_3)_3CNO_2$ with metallic sodium or polarographically, Hoffmann[85,86] obtained in 1961 di-t-butylnitroxyl (XXXVII):

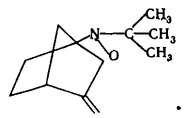


(XXXVII)

In several later studies[87] he made a detailed investigation of the mechanism of this reaction and showed that the primary act of the reduction is the formation of the anion-radical $(CH_3)_3CNO_2^{\cdot-}$ which is then decomposed into NO_2^- and $t\text{-}C_4H_9^{\cdot}$. Recombination of the anion-radical with $t\text{-}C_4H_9^{\cdot}$ leads to the formation of the anion of *NN*-di-t-butylhydroxylamine oxide. The hydrolysis of this salt gives (XXXVII). An analogous mechanism was also proposed for the reactions of tertiary nitroso-compounds with organosodium and organolithium compounds. Several asymmetric nitroxyls were obtained in this way. However, it is noteworthy that the yields of nitroxyls, with the exception of (XXXVII), are extremely low.

The mechanism of reduction of nitro-compounds was also considered by Rassat[88], who used a Grignard reagent[89,90] and $LiAlH_4$ [91,92] as reductants. In studying the reactions of various *para*-substituted nitrobenzenes with t-butylmagnesium chloride[93] the EPR spectra of 22 nitroxyls were recorded, but their structure was judged solely on the basis of the EPR results, which are inadequate.

Rassat and coworkers obtained a stable, optically active nitroxyl (XXXVIII) by the action of t-butylmagnesium chloride on 1-nitrocamphene[94]:

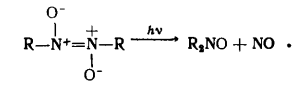


(XXXVIII)

Results have now been obtained[95] which show that not only tertiary but also secondary nitro-compounds can be reduced by this method.

4. Reduction of Nitroso-compounds

In 1964 a group of Japanese investigators described the preparation of nitroxyls in the photolysis of substituted derivatives of nitrosobenzene[96]. Strom and coworkers[97] greatly increased the number of aromatic nitroxyls obtained by this method and found a correlation between the hyperfine splitting constants of the nitrogen atom a_N and the Hammett constant (reviewed by Janzen[98]). Strom and Bluhm[99] assume that the dimer of the nitroso-compound is responsible for the formation of nitroxyls, and that it disproportionates when irradiated:



Despite this assertion a group of Dutch scientists give a strong proof of the formation of nitroxyls directly from the monomeric form[100,101] by the scheme:

$$RNO \xrightarrow{h\nu} R^{\cdot} + NO$$
$$R^{\cdot} + RNO \rightarrow R_2NO^{\cdot}$$

Aliphatic nitroso-compounds form nitroxyls even when irradiated with red light. The formation of nitroxyls also takes place during the thermal decomposition of nitroso-compounds. Tertiary nitroso-compounds thereby yield nitroxyls very readily, but secondary and primary nitroso-compounds require an elevated temperature, which is evidently necessary for the conversion of the dimer into the monomeric form. Ultraviolet irradiation of nitrosoadamantane produced diadamantylnitroxyl[102]. Evidently bistrichloromethylnitroxyl is formed similarly from CCl_3NO.[103]

Photochemical and thermal decomposition of alkyl nitrites evidently also leads to the production of nitroxyls, via the intermediate formation of nitroso-compounds[104-106].

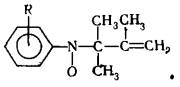
Wajer and coworkers[107] showed that nitroxyls are formed in both the thermal reduction of nitroso-compounds by hydroxylamines[107]:

$$RNO + R'NHOH \rightarrow \underset{\underset{O}{|}}{R-NH} + \underset{\underset{O}{|}}{R'NH}$$

and also in the photochemical reduction of thiophenol[108]:

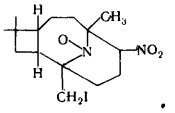
$$2RNO + 2PhSH \rightarrow \underset{\underset{O}{|}}{2R-NH} + PhSSPh$$

In 1966 Sullivan[109] described the production of alkenylarylnitroxyls (XXXIX) by the reaction of nitrosoaryls with 2,3-dimethylbut-2-ene. Here a hydroxylamine is formed as an intermediate, which is oxidised by the nitrosoaryl or by oxygen into the corresponding nitroxyl:



(XXXIX)

Possibly the formation of caryophyllene "iodo-nitrosite" (XL) takes place similarly[110]:



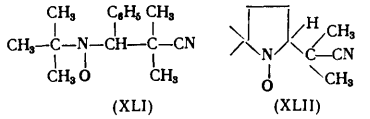
(XL)

As already noted, nitroso-compounds are capable of reacting with active radicals, to form relatively stable nitroxyls. Their ability to do this is now widely used for the collection and establishment of the structure of various radicals formed in polymerisation[111,112], radiolysis[113], photolysis[114,115], and other chemical reactions[101,116-119]. t-Nitrosobutane and nitrosobenzene are most frequently employed as "traps" for radicals.

Nitroxyls are also formed in the reaction of nitrobenzene with stable radicals—triphenylmethyl and 2,4,6-tri-t-butylphenoxyl[120]. A series of aryl-(2-cyanoisopropyl)nitroxyls was obtained by the reaction of nitrosoaryls with the 2-cyanoisopropyl radical[6].

5. Free-radical Addition to Nitrones

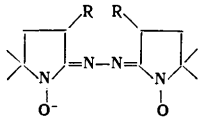
As Brown noted[121], nitrones can give nitroxyl radicals on adding radicals at the double bond. This was confirmed by the experiments of Iwamura and Inamato[122], who obtained the stable nitroxyl (XLI) in 3.2% yield by the reaction of azobutyronitrile with *N*-t-butyl-α-phenylnitrone. The cyclic nitroxyl (XLII) obtained by this method was unstable and rapidly disproportionated in solution:



(XLI) (XLII)

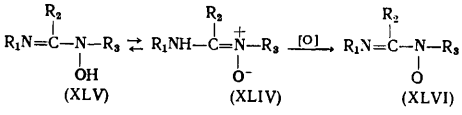
It has been shown[123] that certain nitrones are capable of removing a hydrogen atom from a solvent with the formation of nitroxyl radicals. The ability of nitrones to react with radicals allows them to be used together with nitroso-compounds as "traps" for active radicals[124-126].

Forrester and coworkers[127] described the addition of short-lived radicals to nitrones. They reduced the corresponding azo-1-pyrroline-1-oxide with sodium to give the anion-radical (XLIII)[127]:



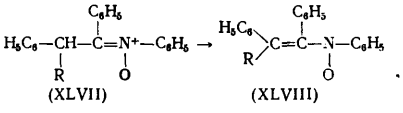
(XLIII)

The oxidation of *C*-aminonitrones (XLIV), which are in tautomeric equilibrium with the corresponding hydroxylamines (XLV), leads to nitroxyls which are stable in solution (XLVI)[128-130].



(XLV) (XLIV) (XLVI)

At the moment the nitrone (XLVII) is produced it is dehydrated with the formation of a derivative of the phenyl(vinyl)nitroxyl (XLVIII)[131]:



(XLVII) (XLVIII)

A survey of the methods of obtaining nitroxyl radicals cannot be concluded without mentioning the old but preparatively convenient method of Meyer[132,133]. In this method oxidation of phenol esters with nitric acid followed by treatment with perchloric acid leads to oxides of diarylammonium salts, reduction of which gives the nitroxides.

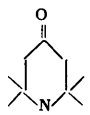
Selective specific reactions of radicals which do not involve the free valency are widely used for obtaining various functional derivatives of nitroxyls[134]. This method of preparation will be discussed in Section III.

III. CHEMICAL PROPERTIES OF NITROXYL RADICALS

1. Decomposition and Stability of Nitroxyls

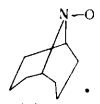
Thermochemical data[135,136] show that the gain in energy of the delocalisation of an electron for the N–O fragment is ~ 30.4 kcal mole^{-1} for heterocyclic nitroxyls.

It is remarkable that 2,2,6,6-tetramethyl-4-oxo-1-piperidyl radical (XLIX)[137] is unstable owing to the impossibility of delocalisation of the unpaired electron.



(XLIX)

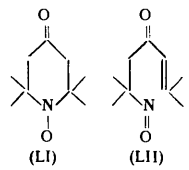
Many heterocyclic amines form nitrones on oxidation[138-141]. Oxidation of heterochain amines leads, through the intermediate formation of nitroxyls, to nitrones[30]. In 1956 Rogers and coworkers[142] proposed that nitroxyl radicals would be stable if their nitrogen atom was framed by tertiary α-carbon atoms, since then the formation of a nitrone would be excluded. Subsequent work showed that actually the absence of α-hydrogen atoms ensures the stability of the nitroxyls. The bicyclic nitroxyls (L)[143], (XXVIII)[72], and (XXXIII)[76], which have α-hydrogen atoms, cannot form nitrones without destruction of a ring owing to Bredt exclusion[144] and therefore should be stable:



(L)

The stability of the nitroxyl (XLI) is explained by the impossibility of its disproportionating to form a nitrone owing to steric hindrance in the region of the reaction centre[122]; the analogous cyclic radical (XLII) is unstable.

According to Murayama[145], the relative instability of (LI) is the result of the carbonyl group activating the hydrogen atoms in position 3 and 5 of the piperidine ring and the radical disproportionating with formation of nitrogen(II) oxide, phorone—of which the nitroso-compound (LII) is a precursor—and 2,2,6,6-tetramethyl-1-hydroxy-4-oxopiperidine:



(LI) (LII)

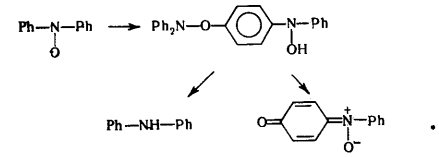
When irradiated for 15 h the nitroxyl (XIII) decomposes according to the first-order law with formation of the diene (LIII) and probably nitrogen(II) oxide[146]. Photolysis of other nitroxyls proceeds only when the radiation is more prolonged:

(LIII)

Photolysis of biradicals also leads to their destruction[147], the EPR spectrum of the biradical being transformed initially into the spectrum of a monoradical and only then does the EPR signal of the monoradical start to disappear.

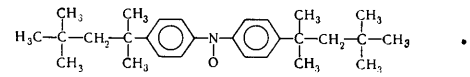
Thermogravimetric investigation of silicon-containing bi- and mono-radicals shows[147] that all these compounds, irrespective of molecular weight and structure, decompose at 195°C with evolution of heat and a decrease in the weight of the specimen.

The decomposition of aromatic radicals was first studied by Wieland and Roth[12], who showed that diphenylnitroxyl disproportionates into diphenylamine and quinone imine oxide:



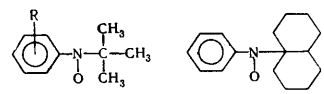
Subsequently an analogous disproportionation was observed with 4,4'-dichlorodiphenylnitroxyl[77]. Aryl alkyl nitroxyls[20,148] and the nitroxyls of the tetrahydroquinoline series[65] decompose similarly, and in the decomposition of certain 4-alkylphenyl-t-butylnitroxyls dimers and trimers were isolated[20].

The most stable series of diarylnitroxyls are 4,4'-dianisylnitroxyl[12,132], 4,4'-dinitrodiphenylnitroxyl[12], 2,2'-dimethyl-4,4',6,6'-tetramethoxydiphenylnitroxyl[132], and the nitroxyl (LIV)[149]; the most unstable are 4,4'-ditolylnitroxyl[11,12]; 2,2',4,4'-tetramethoxydiphenylnitroxyl[132,133], and diphenylnitroxyl[12]. The stability of (LIV) can probably be explained by steric hindrances to dimerisation according to Wieland's scheme:



(LIV)

In studying aryl-t-butylnitroxyls (LV) Calder and Forrester[150] concluded that their somewhat greater stability in comparison with phenyl-t-butylnitroxyl is due to steric factors.



(LV) (LVI)

A noteworthy fact is that unlike phenyl-t-butylnitroxyl (LV; R = H) the structurally similar phenyl-*trans*-decalylnitroxyl (LVI)[15] and the Kenyon–Benfield radical (IV)[18] are stable.

It has been shown[151] that an increase in the stability of the nitroxyls of the hydrogenated quinoline series can be achieved by the introduction into position 2 of the heterocycle of two methyl groups of the geminal type. The introduction of a spiran cyclohexyl screen in this position of the heterocycle sharply increases the stability of the nitroxyls of the hydrogenated quinoline and benzoxazine series[59-61].

The decomposition products and stability of the α-nitronylnitroxyls (XVIII) was not investigated, but it is noteworthy that radicals with alkyl substituents are less stable than those with aromatic[34,35].

2. Redox Reactions of Nitroxyls

Usually the presence not only of an electron donor but also a proton donor is necessary for the reduction of nitroxyls. This evidently explains the stability of nitroxyls in relation to the alkali metals[87].

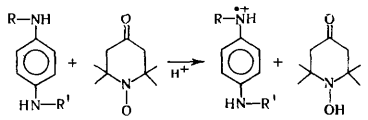
The nature of the products of the reduction of nitroxyl radicals depends on the reductant used or, in hydrogenation with hydrogen, on the catalyst. In the presence of platinum catalyst Adams hydrogenation leads exclusively to the formation of the corresponding hydroxylamines both

for monoradicals [57,84,152,153] and for polyradicals [63]. The use of Raney nickel catalyst leads to the formation of amines [62,154]. Here the reaction proceeds through the stage of formation of hydroxylamine. Reduction with tin(II) chloride in hydrochloric acid [12], zinc in acetic acid [13], and hydrogen iodide also lead to amines [11]. The last reaction enables nitroxyls to be titrated iodometrically [155]. Bistrifluoromethylnitroxyl reacts with gaseous HCl and HBr with the formation of hydroxylamine [23,156]. Phenylhydrazine [12], hydrazine [157], lithium tetrahydroaluminate [158], and formic acid [159] reduce nitroxyls to hydroxylamines. (Lithium tetrahydroaluminate does not reduce the nitroxyl group of the radicals of the hydrogenated pyrrol series [160].) Hydrazobenzene is also a strong reductant of nitroxyl radicals [161]. Kinetic investigation allows the following scheme of reduction to be proposed:

$$>N\dot{-}O + Ph{-}NH{-}NH{-}Ph \rightarrow Ph{-}\dot{N}{-}NH{-}Ph + >N{-}OH$$
$$>N\dot{-}O + Ph{-}\dot{N}{-}NH{-}Ph \rightarrow Ph{-}N{=}N{-}Ph + >N{-}OH\,.$$

In the polarographic reduction of nitroxyls at the dropping mercury electrode [162] hydroxylamines are formed, transfer of an electron preceding the protonisation of the radical.

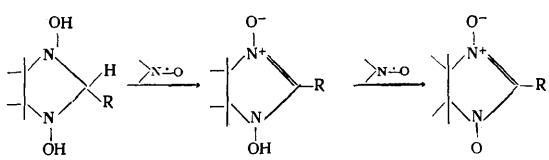
Nitroxyl radicals are widely used in chemistry as mild one-electron oxidants. Thus in acid medium the reaction of nitroxyls with substituted *p*-phenylenediamines leads to the formation of stable cation-radicals [163,164]:



Phenols are oxidised by nitroxyls to quinones [165]; sterically hindered phenols form stable phenoxyl radicals [166].

Nitroxyls of the piperidine series oxidise Fe^{2+} to Fe^{3+}, thereby being converted into hydroxylamines [167]. Interestingly, nitroxyls of the isoindoline and pyrrolidine series do not react with Fe^{2+}. Nitroxyls are also reduced to hydroxylamines by dihydropyridines [168,169] and plastoquinones [170].

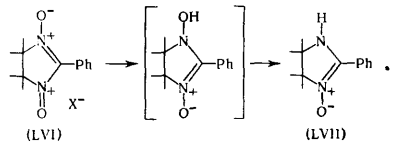
α-Nitronylhydroxylamines are oxidised by nitroxyl radicals to the corresponding α-nitronylnitroxyls [34]:



Nitroxyls are capable not only of accepting electrons but also of donating them, forming highly reactive salts of an immonium oxide $>\overset{+}{N}{=}O,\ X^-$. [34,132,158] To avoid further conversions of the salts of the immonium oxide the oxidation is carried out in an inert medium, using chlorine or bromine as oxidant. Unlike chlorine [171], the use of bromine usually leads to perbromides [172]. Biradicals form salts of an immonium oxide just like monoradicals [158,171,172]. The salts of immonium oxides oxidise primary alcohols to aldehydes and secondary alcohols to ketones, thereby being converted into hydroxylamines. This process can proceed both by a radical and by an intramolecular cyclic mechanism [158]. Nitroxyl halides react violently with tertiary amines with the formation of the amine hydrohalide and a nitroxyl radical. A cation-radical of the amine is formed as an intermediate [158]. Iodometric titration of immonium oxide salts leads to hydroxylamines [158]:

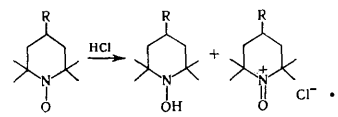
$$>\overset{+}{N}{=}O \xrightarrow{\bar{e}} >N\dot{-}O \xrightarrow[H^+]{\bar{e}} >N{-}OH\,.$$

Immonium oxide salts oxidise aqueous alkali to hydrogen peroxide [35] and are reduced by water to the initial nitroxyl [158]. Boiling (LVI) in alcoholic solution leads to the amine (LVII) through the intermediate formation of a hydroxylamine [35]:



(LVI) (LVII)

Under the action of dry hydrogen chloride, nitroxyls disproportionate according to the scheme [158]:



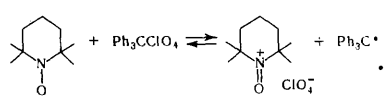
The Kenyon–Benfield radical also reacts [18]. Under the action of dry hydrogen chloride di-t-butylnitroxyl (XXXVII) forms hydroxylammonium chloride [86].

Under the action of acids, nitroxyls rapidly disproportionate [35,158]; the first stage of this process is the reversible protonisation of the nitroxyl group [173,174]:

$$>N\dot{-}O \underset{-H^+}{\overset{+H^+}{\rightleftharpoons}} >\overset{+}{N}\dot{-}OH\,.$$

Aprotic acids act specifically on the ketone-radical (LI). The radical disproportionates into hydroxylamine and immonium oxide salt, which decomposes with the formation of the nitroso-compound (LII) [175]. [As already noted [145], the thermal decomposition of the ketone radical also leads to (LII)]. To explain this process it is not necessary to assume the existence of an ion–radical equilibrium in the solution of the nitroxyl.

Reaction of nitroxyls with Ph_3CClO_4 in the presence of oxygen leads to a salt of the immonium oxide [176]:



This process is complicated by the decomposition of Ph_3CClO_4 with the formation of $HClO_4$ under the action of which the nitroxyl disproportionates as usual.

Nitroxyls of the piperidine series are oxidised by Cu^{2+} ions in methanol solution [159]. This reaction does not take place in water. Interestingly, a reduction product of the radical is formed finally—hydroxylamine, probably as a result of the transfer of a hydride ion from methanol to the oxidised form of the radical:

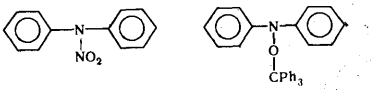
$$>N\dot{-}O + Cu^{2+} \rightarrow >\overset{+}{N}{=}O + Cu^+$$
$$>\overset{+}{N}{=}O + CH_3OH \rightarrow >N{-}OH + \overset{+}{C}H_2OH$$
$$\overset{+}{C}H_2OH \rightarrow CH_2O + H^+\,.$$

A similar process is observed in the reaction of 2,2,6,6-tetramethyl-1-hydroxypiperidine with $Cu(ClO_4)_2$ in triethyl orthoformate solution [177]. In this instance a reduction product of the nitroxyl is also formed—2,2,6,6-tetramethylpiperidine.

Di-t-butylnitroxyl (XXXVII) is capable of promoting the catalytic oxidation of methanol into formaldehyde[178] and is involved in the redox cycle.

3. Radical Reactions of Nitroxyls

Nitroxyls, like all radicals, undergo recombination. (Nitroxyls do not recombine amongst themselves, except for bistrifluoromethylnitroxyl[22]). Diphenylnitroxyl recombines with nitrogen(II) oxide and with triphenylmethyl to form the corresponding derivatives (LVIII) and (LIX)[18].



(LVIII) (LIX)

4,4'-Dinitrophenylnitroxyl is formed with nitrogen(IV) oxide. As Wieland and Roth showed[12], this reaction takes place with saturation of the free valence and with subsequent oxidation of the hydroxylamine formed.

The recombination of diphenylnitroxyl with 2,4,6-tri-t-butylphenoxyl has also been described[179].

Owing to the presence of bulky substituents near the reaction centre, non-aromatic nitroxyls do not react with triphenylmethyl[176] or 1,1-diphenyl-2-picrylhydrazyl[159].

The reaction of nitroxyls with 2-cyanoisopropyl radical, obtained in the decomposition of azoisobutyronitrile, leads to the *O*-2-cyanoisopropylesters of hydroxylamines[159,180].

The presence of phenyl radicals in the system also leads to the corresponding esters, as is observed as side reactions in the reduction of nitroxyls with phenylhydrazine[153].

Nitroxyls are capable of reacting with thiyl radicals formed from benzenethiols[181], thiamine disulphide[182], and tetramethylthiuram disulphide[183].

Aromatic nitroxyls react with both alkyl and peroxide radicals, whereas non-aromatic ones react only with alkyl radicals[184,185], which allows them to be used as acceptors of alkyl radicals[186].

The ability of nitroxyls, in reacting with active radicals, to break radical chains allows them to be used as inhibitors of the radical polymerisation of tetrafluoroethylene[187], chloroprene[188], styrene[189], and 2-vinylpyridine[190]. Nitroxyls can be used as inhibitors for the thermal oxidative destruction of polyamines[191,192], polypropylene[193,194], and polyformaldehyde[194,195], as inhibitors of the photo- and thermodegradation of polyethylene[196] and of poly(vinyl chloride)[197]. Nitroxyls inhibit the autoxidation and polymerisation of styrene[198]. In studying the inhibition of the polymerisation of α-methylstyrene it was shown[199] that the reactivity of the biradicals differs significantly from that of monoradicals.

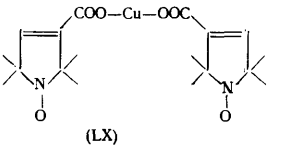
At elevated temperature nitroxyls are capable of removing hydrogen from hydrocarbons[200]. The reactivity of biradicals and polyradicals in reactions involving the removal of hydrogen depends significantly on the spin–spin exchange between the paramagnetic fragments[201].

Kreilick and Weissman[202] observed by the NMR method that in a solution containing a nitroxyl radical and the corresponding hydroxylamines, hydrogen rapidly migrates from the hydroxylamine to the radical. This process resembles the Wieland exchange reaction[13], where the reaction of diphenyl nitroxyl and tetra(methoxyphenyl)-hydrazine leads to di(methoxyphenyl)nitroxyl and tetraphenylhydrazine.

Specific addition reactions of bis(trifluoromethyl)nitroxyl[23,24,156,203–206] will not be discussed in the present review.

4. Complex Formation

The copper salt of 3-carboxy-2,2,5,5-tetramethyl pyrroline-1-oxyl[207] (LX):



(LX)

is diamagnetic, unlike the true biradicals and copper(II) salts, which shows the formation of a complex with participation [in spin pairing (Ed. of Translation)] of the unpaired electrons of both nitroxyl groups and copper ion. Similar complexes with metals of variable valence are formed by paramagnetic Schiff bases[208,209] and xanthogenates[210].

On reacting with palladium salts, di-t-butylnitroxyl (XXXVII) forms the diamagnetic complexes $XPd[ONC(CH_3)_3]_2$.[211] With cobalt halides, (XXXVII) forms paramagnetic complexes which dissociate on dissolution[212].

2,2,6,6-Tetramethylpiperidine-1-oxide forms complexes[177] on reacting with the perchlorates of Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, and Cu^{2+}. Nitroxyls form stable complexes with Lewis acids[213,214] and the EPR spectrum shows splitting from the magnetic nuclei of aluminium (for AlX_3) and gallium (for GaX_3).

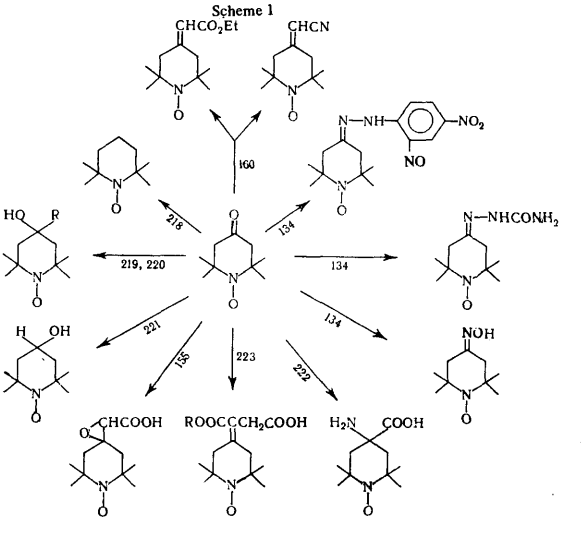
5. Reactions without Use of the Free Valence

The presence in many nitroxyls of the hydrogenated pyridine and hydrogenated pyrrole series of a second functional group separated from the radical centre by a chain of σ-bonds, and the reliable steric screening of the nitroxyl group allowed a class of reactions new in principle to be effected—reactions of radicals without use of the free valence[53,134,215].

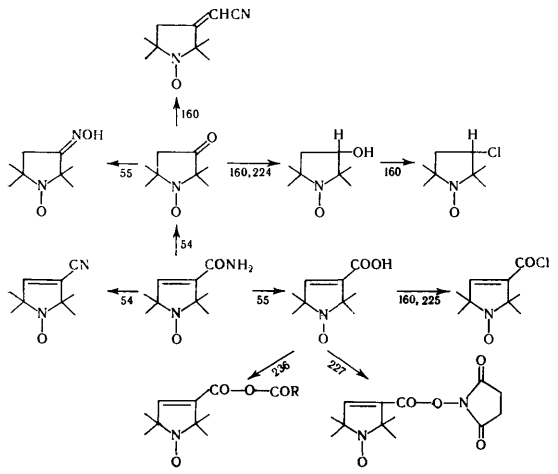
As already noted[216], it is possible that certain reactions of porphyrexide (I) proceed without participation of the unpaired electron, but experimental proof of this has not yet been obtained.

The scheme advanced by Forrester[217] for the reaction of chlorine with (I) is subject to doubt since it was not confirmed experimentally.

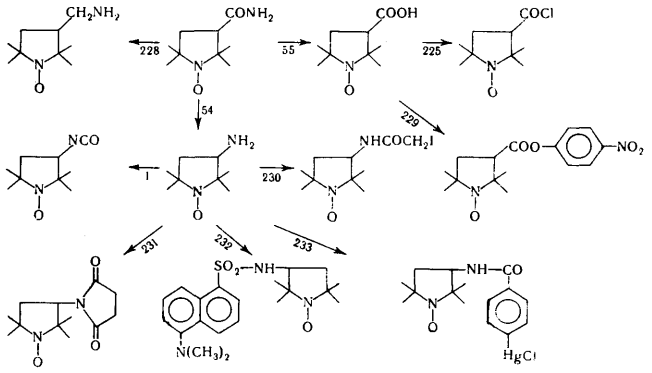
Scheme 1



Scheme 2



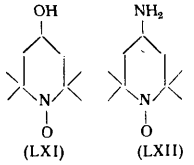
Scheme 3



Schemes 1–3 give an idea of the synthetic possibilities of reactions of radicals not involving the unpaired electron. It is noteworthy that the insignificant yield of paramagnetic products in the reduction of the ketone-radical (LI) with hydrazine and in its reaction with ethylmagnesium bromide undoubtedly show the dominating role in this instance of trivial reactions involving the unpaired electron.

The application to five- and six-membered ketone-radicals of the modified Wittig reaction[234] allowed the corresponding acid- and aldehyde-radicals to be synthesised[160]. However, not all the stages of this preparation are reactions without participation of the unpaired electron.

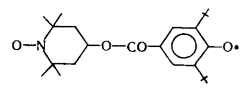
This type of reaction, first effected with ketone-radical (LI), was subsequently extended to other bifunctional nitroxyls. Six- and five-membered hydroxy- and amino-radicals were especially promising in this respect:



(LXI) (LXII)

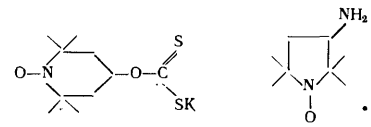
The method of preparation of paramagnetic esters most usually employed is the condensation of an alcohol radical (LXI) with acid chlorides[53,235-237]. In the reaction of alcohols with acid chlorides, hydrogen chloride is released, under the action of which the nitroxyls disproportionate. To avoid this the reaction is carried out in the presence of tertiary amines. As well as acid chlorides, anhydrides[157] and carboxylic acids can be used for the synthesis of paramagnetic esters; in the latter instance dicyclohexylcarbodi-imide was used as condensing agent[228,238]. Reaction of the alcohol-radical (LXI) with the chlorides of dicarboxylic acids leads smoothly to biradicals[239-242]. This method is general for the preparation of polyradicals[242-244]. A series of individual polyradicals was prepared under the action on pyridine solutions of pyrocatechol, hydroquinone, and phloroglucinol of 2,2,5,5-tetramethyl-1-hydroxypyrroline-3-carbonyl chloride[225].

By the action on the alcohol-radical (LXI) of 3,5-di-t-butyl-4-hydroxybenzoyl chloride with subsequent dehydrogenation of the phenol, mixed nitroxyl–phenoxyl biradical (LXIII) was obtained:



(LXIII)

In addition to organic acid chlorides, phosphorus, sulphur and silicon chlorides can be used for obtaining polyradicals[243-247]. Nitroxyl analogues of esters of phosphorus acids were synthesised in this way[248-250]. The alcohol radical (LXI) reacts smoothly with isocyanates. Both monoradicals[53] and polyradicals[239] can be obtained in this way[239]. The reaction of an alcohol-radical with carbon disulphide in alkali leads to the xanthogenate (LXIV), which forms the corresponding biradical under the action of iodine[210]:



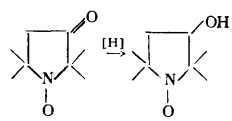
(LXIV) (LXV)

The reaction of the amine-radicals (LXII) and (LXV) with acid chlorides enables a large number of a variety of paramagnetic amides to be obtained[235,236]. The reaction of the amine-radical (LXII) with aromatic aldehydes leads to paramagnetic Schiff bases[208]. The action of di-isocyanates on (LXII) gave the corresponding biradicals[251].

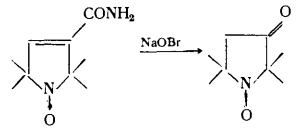
Reactions which do not involve a free valence allowed paramagnetic polymers to be prepared. Thus, the reaction of the alcohol-radical (LXI) with the acid chloride of poly(acrylic acid) leads to the formation of a paramagnetic polymer with a lattice structure[252]. Another approach has also been employed[253]. A paramagnetic polymer is obtained by the polymerisation of the 2,2,6,6-tetramethyl-1-hydroxy-4-piperidine ester of methylacrylic acid.

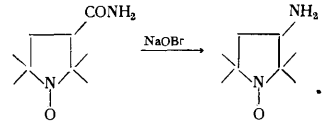
A paramagnetic polymer is also formed in the reaction of sulphur dichloride with diallyl-(2,2,6,6-tetramethyl-1-hydroxy-4-piperydyloxy)silane[254].

Reactions of radicals not involving the use of the free valence can assist in the preparation of nitroxyls which are almost impossible to obtain by other methods. For example, 2,2,5,5-tetramethyl-3-hydroxypyrrolidine 1-oxide cannot be obtained by direct oxidation of an amine, but it is readily obtained by the reduction of 2,2,5,5-tetramethyl-3-oxopyrrolidine 1-oxide with aluminium isopropoxide[255].

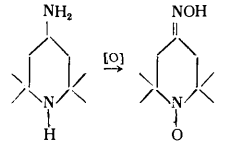


It is also impossible to obtain 2,2,5,5-tetramethyl-3-oxopyrrolidine 1-oxide and 2,2,5,5-tetramethyl-3-aminopyrrolidine 1-oxide by direct catalytic oxidation but they were obtained by the following scheme[54]:



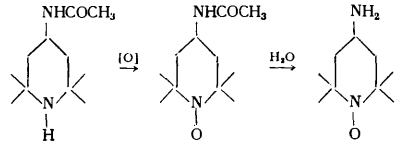


Catalytic oxidation of 2,2,6,6-tetramethyl-4-aminopiperidine with hydrogen peroxide leads to the oxime-radical (LXVI):



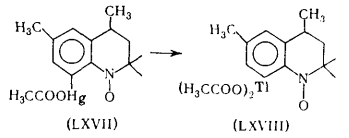
(LXVI)

The amine-radical (LXII) can be obtained by the following scheme[52]:



(LXII)

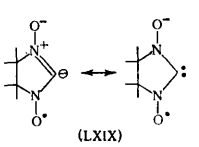
In studying the reaction of the organomercury nitroxyl (LXVII) with thallium(III) isobutyrate replacement of mercury by thallium was observed, with the formation of the organothallium nitroxyl (LXVIII)[256]:



(LXVII) (LXVIII)

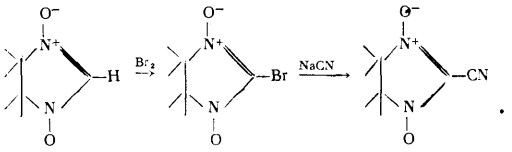
This reaction is evidently an example of a reaction without participation of free valence radicals with a strongly delocalised unpaired electron.

Reactions which do not involve a free valence are also observed in the α-nitronylnitroxyl series (X). Thus (X; R = H) in D_2O rapidly exchanges hydrogen for deuterium[35]. In alkaline media this process takes place with the formation of the anion-radical (LXIX), the existence of which in a solution of potassium dimethylsulphoxide-t-butyoxide was confirmed by the EPR method:

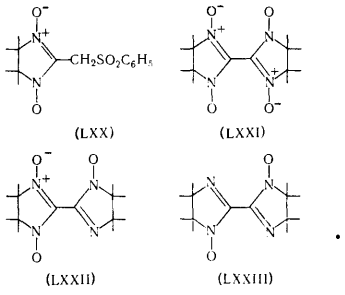


(LXIX)

Replacement of hydrogen by halogen, and then of halogen atoms by hydroxy- and cyano-groups was effected in the α-nitronylnitroxyl series[257]:



Sulphones (LXX)[258] and the conjugated biradicals (LXXI), (LXXII), and (LXXIII)[259] were obtained by such reactions which do not involve the free valence:



(LXX) (LXXI)

(LXXII) (LXXIII)

The change in the form of the EPR spectra of the biradicals on varying the distance between the paramagnetic fragments in conjugation with reactions not involving the free valence can be used for finding the spatial configuration of organic molecules[260].

For example, in the reaction of 2,2,6,6-tetramethyl-4-hydroxypiperidine 1-oxide with the acid chlorides of *cis*- and *trans*-cyclopropanedicarboxylic acids, the corresponding *cis*- and *trans*-esters of these acids were obtained. The *cis*-biradical exhibited a five-component EPR spectrum, which showed the proximity of the two paramagnetic centres. The three-line spectrum of a *trans*-biradical shows the lack of interaction through space of the unpaired electrons, as a result of which electronic exchange is absent.

The discovery and development of the reactions of radicals without involvement of the free valence allowed a new method of investigation to be created, widely used in biochemistry, biophysics, and molecular biology, the so-called "spin-label" method, (see reviews elsewhere[261,262]).

The development of this method, stimulated by the brilliant studies of McConnell, has proceeded in two directions. The first is connected with spin-labelled biomolecules, for example, albumens[263-267], nucleic acids[227,268,269], lipids[270-273], etc. The second direction is the synthesis of paramagnetic analogues and models of physiologically active compounds[78,228,249,250,274,275].

The ability of nitroxyls to migrate in polymers[276] allowed a new method of investigation of molecular motions in polymers[277-279], liquids[280], and biopolymers[281,282] to be investigated—the so-called "spin-probe" method.

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Electrophilic Substitution in Cyclopentadienide Anions

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The considerable new synthetic possibilities, which have arisen as a result of studies on electrophilic substitution reactions in the cyclopentadienide series, are considered in the review. The possible mechanism of these processes is analogous to the mechanism of substitution in the benzene series. Much attention has been devoted to the problem of the direction of electrophilic attack in cyclopentadienide ions containing both electron-donating and electron-accepting substituents. The bibliography includes 63 references.

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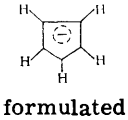
I. INTRODUCTION

The problem of electrophilic substitution has been most widely studied in the benzene series. However, recently the attention of investigators has been increasingly drawn to problems associated with the study of electrophilic substitution in other aromatic systems, in particular such as the cyclopentadienide ion (CPD ion). The interest in this problem arises mainly from the synthetic requirements which must be met in various substituted cyclopentadienides necessary for the preparation of fulvenes, ylides, sandwich π complexes with transition metals, and many other derivatives. The elucidation of the question of the direction of the electrophilic attack is of particular interest in this problem, since, in contrast to benzene, the cyclopentadienide ion is a non-alternant system.

II. AROMATIC PROPERTIES OF CYCLOPENTADIENIDE IONS

As early as 1901, it was known as a result of Thiele's work [1] that cyclopentadiene exhibits acidic properties†. Thiele found that the potassium salt of cyclopentadiene is fairly stable although very reactive. The high stability of the $C_5H_5^-$ ion was repeatedly confirmed subsequently. In 1928 Goss and Ingold [3] explained the reason for the stability of salts with cyclopentadiene ions by the fact that the six π electrons distributed over the five-membered ring form in this ion an aromatic system resembling that of benzene. On the basis of LCAO-MO calculations, Hückel [4,5] suggested that the cyclopentadienide anion is a stable system, since all four π electrons of the two double bonds and the lone electron pair of the carbon atom remaining after the abstraction of a proton are involved in cyclic conjugation. The negative charge of the cyclopentadienide ion is not localised at an individual carbon atom but is distributed throughout the ion. All the π electrons are located in bonding orbitals, forming a "closed" electron cloud.

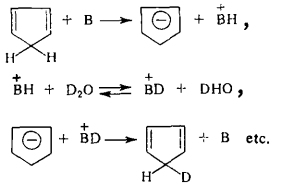


At the same time Hückel formulated the rule of aromaticity.

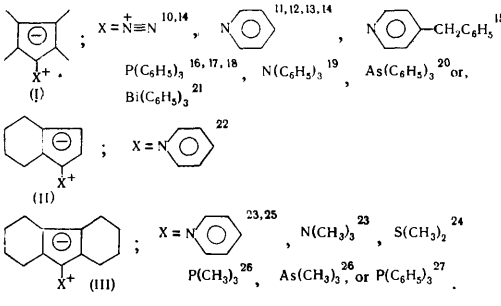
†According to the latest data, $pK = 15$ for cyclopentadiene [2].

Tkachuk and Lee [6] showed experimentally by a tracer atom method (^{14}C) that all five carbon positions in the cyclopentadienide anion are equivalent. Moreover, the equivalence of all five C–C and C–H bonds in the cyclopentadienide ring was demonstrated by X-ray diffraction, electron diffraction, and also spectroscopic methods [7]. The resonance energy for this ion proved to be 48 kcal mole^{-1}. [8]

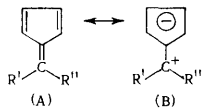
In a study of deuterium exchange in cyclopentadiene, Kursanov and Parnes showed that, in the presence of a base, all six hydrogen atoms are very readily exchanged for deuterium [9]. They also explained this finding by the aromatic properties of the cyclopentadienide ion:



Not only salts with alkali metals and magnesium but also saltlike dipolar compounds containing an organic cation linked by covalent bonds to the cyclopentadienide ion, the so called ylides, are known for cyclopentadienide ions. Usually ylides are unstable compounds but the introduction of the stable aromatic cyclopentadienide ion allows their isolation in a pure form. A wide variety of ylides incorporating cyclopentadienide (type I), indenide (type II), and fluorenide (III) anions linked to the cationic component containing exo- or endo-cyclic atoms of the 'onium-forming elements in Group V (nitrogen, phosphorus, arsenic, antimony and bismuth) and partly Group VI (sulphur) are now known [10–27]:



The study of the dipole moments of certain ylides confirmed their high polarity[28,29]. Fulvenes can be regarded as to some extent of the same type. Their dipole moment is about 1.5 D [30] and the resonance energy is 12 kcal mole^{-1} [31] (i.e. one-third of the resonance energy of benzene). The π-electronic structure of fulvenes can be described by the resonance hybrid of the covalent structure (A) and the polar structure (B):



(A) (B)

where R′ = R″ = H, alkyl, or aryl.

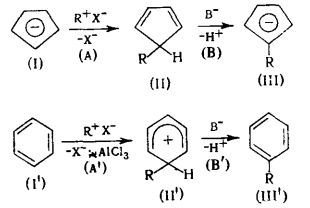
As the electron-donating properties of the substituent at the C_6 carbon atom become more pronounced, the contribution of the polar structure to the resonance hybrid increases. The appreciable contribution of the polar structure is explained, in accordance with Hückel's rule [4,5], by the stability of the cyclic system containing six π electrons.

In contrast to the salts of the cyclopentadienide anion with alkali metals, magnesium, and ammonium cations, the derivatives with transition metal cations lose their ionic properties in most cases. The exceptions will be discussed below. An unusual type of bond, which has been called the π-complex bond, arises under these conditions. The compounds formed, among which ferrocene, nickelocene, and cobaltocene have been most thoroughly investigated, are fairly stable, particularly ferrocene. Dative bonds formed with the *d* electrons of the transition metal make a significant contribution to bond stabilisation in these compounds, in addition to the donor–acceptor bonds.

III. REACTIONS WITH ELECTROPHILIC AGENTS

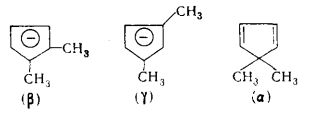
The availability of various cyclopentadienide ions is to some extent limited by the availability of the corresponding cyclopentadienes. The latter may be obtained mainly by two methods: by synthesising the five-membered ring via a cyclisation reaction and by electrophilic substitution in the already existing cyclopentadienide ion. The first method has no direct bearing on the problem under consideration; it is discussed in a useful review by Moritani and Fujiwara [32]. Another method of synthesis, based on the reaction with electrophilic reagents‡, has begun to be developed comparatively recently. It has a number of advantages over the first procedure, since it makes it possible to obtain very complicated derivatives of the cyclopentadienide ion in one or two stages, but, on the other hand, the method is complicated by the formation of side products and involves the necessity to elucidate the direction of electrophilic attack.

The mechanism of electrophilic substitution in the cyclopentadienide ion (stages A and B) is formally similar to the mechanism of electrophilic substitution in the benzene series (stages A′ and B′).[33,34] It is postulated that undissociated cyclopentadienes (II) correspond to the σ complex (II′) in the benzene series:



When various electrophilic agents are employed, the final result in the cyclopentadienide series depends as a rule on whether the substituent introduced is electron-donating or electron-accepting. Since electron-donating substituents increase the electron density of the ring, their introduction results in an increase of the nucleophilicity of the cyclopentadienide ion and, in the presence of sufficient electrophilic agent, it is possible to achieve complete substitution of hydrogen atoms in the initial cyclopentadiene. It is noteworthy that polysubstituted products are obtained even when the initial reactants are employed in 1 : 1 proportions, since some of the cyclopentadienide ions are consumed as a base, as a result of which a certain amount of unsubstituted cyclopentadiene is isolated from the reaction mixture. On the other hand, the introduction of very powerful electron-accepting substituents lowers the nucleophilicity of the cyclopentadienide ion and therefore, under the usual conditions, it is possible as a rule to substitute only two or three hydrogen atoms. Special conditions must be employed to achieve complete substitution.

The cyclopentadienide ion can enter into electrophilic substitution reactions even with weak electrophilic agents such as methyl iodide. Thus in 1965 McLean and Haynes [33,34] showed that, depending on the reaction conditions, different mixtures of products are formed. In liquid ammonia in the presence of a deficiency of a base ($NaNH_2$) the reaction can stop at the monomethylation stage. With increase of the methyl iodide: sodium cyclopentadienide ratio, the yield of polymethylated cyclopentadienes rises. A methyl substituent in the ring has a significant influence on the direction of attack. Two isomers (β and γ) are possible for dimethylcyclopentadienide ions. It has been found that the ratio of the disubstituted β- and γ-derivatives is 3.5 : 1:

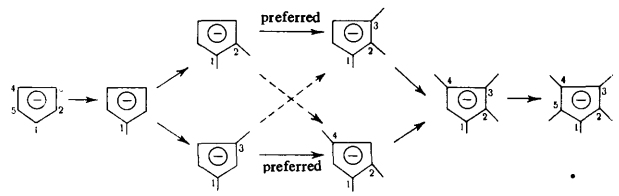


(β) (γ) (α)

It is noteworthy that the ratio of the β- and γ-isomers was determined by analysing a mixture of the corresponding dimethylcyclopentadienes by gas–liquid chromatography. The analysis revealed the presence in the mixture also of a small amount (about 1%) of a product with the second methyl group in the α-position. Thus the selectivity series for attack in the methyl cyclopentadienide ion is $\beta > \gamma > \alpha$. It was discovered that the α-position is approximately 5 times less sensitive to attack by the electrophilic agent than even the γ-position. Since the resulting selectivity series for electrophilic attack corresponds to the distribution of electron density in the methyl cyclopentadienide anion [calculated by Hückel's method (Fig. 1)], the authors suggested that the site of electrophilic substitution in the cyclopentadienide ion may be determined by the distribution of electron density in the ring [33].

‡In the present review we are not considering the reactions of the cyclopentadienide ion with electrophilic agents such as the halides of a number of elements (silicon, tin, mercury, etc.), since the description of such data, closely related to the field of metallotropic reactions, would unduly divert the reader's attention from the main topic.

For the same reason, on further methylation the derivatives obtained from 1,2-dimethyl- and 1,2,3-trimethyl-cyclopentadienide ions predominate over the product which might have been expected from 1,3-dimethyl- and 1,2,4-trimethyl-substituted ions:



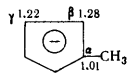
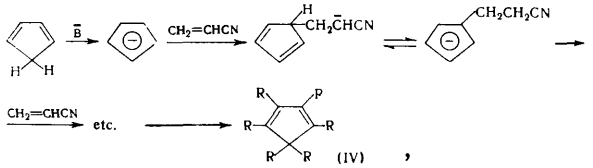


Figure 1. Distribution of electron density in the methylcyclopentadienide ion[33].

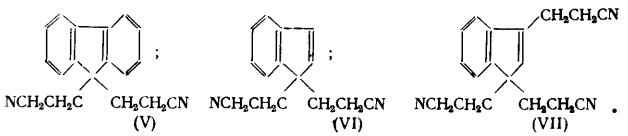
However, Akhrem, Mironov et al.[35], who also made a study of the methylation of sodium cyclopentadienide, note that, when tetramethylcyclopentadienides are employed in this reaction, the *gem*-disubstituted diene is formed in considerable amounts. They believe that in polymethylated cyclopentadienides the site of further alkylation is determined by the operation of factors other than those in the lower homologues.

Another interesting reaction which leads to a substitution product is the cyanoethylation of cyclopentadiene in the presence of a base (benzyltrimethylammonium hydroxide). Unfortunately the details of this reaction have been little investigated, but it is known that, even for equimolar proportions of cyclopentadiene and acrylonitrile, the hexacyanoethylated product (IV) is formed in considerable amounts[36]. The catalytic properties of the base, which are required only to initiate the reaction, are employed:

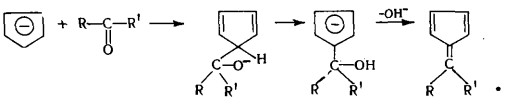


where R = CH_2CH_2CN.

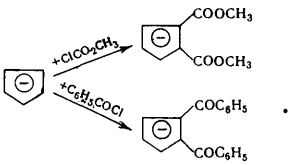
Under the same conditions, fluorene gives the dicyanoethylated product (V) and the reaction of indene with acrylonitrile leads to the dicyanoethylated product (VI) and crystalline tris-(β-cyanoethyl)indene (VII):



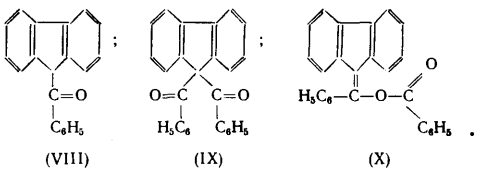
The reaction of aldehydes and ketones with cyclopentadienide ions constitutes the basis of a well known method for the synthesis of fulvenes[37]. The secondary process involving the elimination of the OH ion with formation of the fulvene system completes this reaction:



On the other hand, when electrophilic agents such as methyl chlorocarbonate[38] and benzoyl chloride[39] are employed, the substitution stops at the stage of disubstituted products and in this case, as in the reaction with methyl iodide, the second substituent enters at the β-position relative to the first and the initial cyclopentadienide ion plays the role of a base:

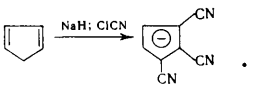


It is noteworthy that lithium fluorenide is also readily benzoylated to a mixture of monobenzoylfluorene (VIII), 9,9-dibenzoylfluorene (IX), and 9,1'-benzoyloxybenzylidenefluorene (X). The relative amounts of the products depend on the nature of the metal and the solvent[40]:

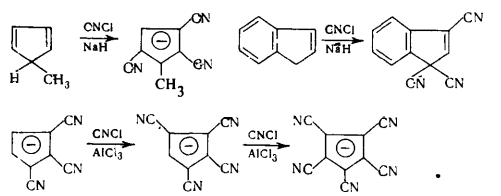


The reaction with cyanogen chloride has been most thoroughly investigated; by this process in the presence of NaH, Webster[41] achieved the substitution of cyano-groups in cyclopentadienides[41].

In contrast to alkyl substituents, the introduction of groups such as CN into the cyclopentadienide ion reduces its nucleophilic activity and therefore the reaction may be stopped at each stage in the presence of a limited amount of cyanogen chloride:



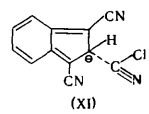
The reaction with cyclopentadiene, methylcyclopentadiene, and indene stops at the stage of the tricyano-product, while tetra- and penta-cyano-derivatives can be obtained from the tricyano-ion only when a Friedel–Crafts catalyst is employed:



The cyano-group is substituted in the tricyanomethylpentadienide anion in the presence of aluminium chloride with formation of tetracyanomethylcyclopentadienide.

In indene the third cyano-group attacks the carbon atom linked to a cyano-group and not a vacant position.

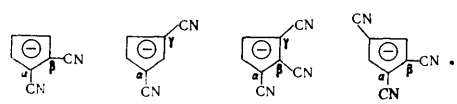
The explanation is that the energy of the transition state (XI) (of the *o*-quinodimethane type) formed on introduction of a cyano-group in a vacant position should be higher:



(XI)

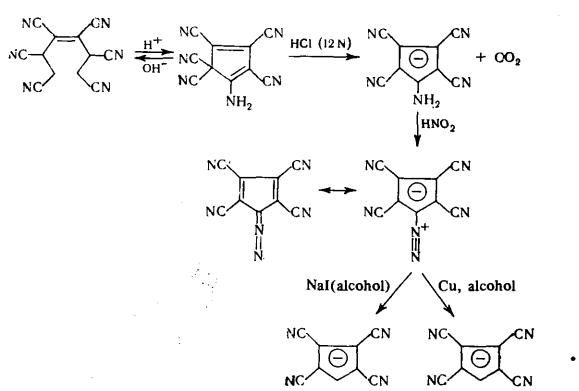
Each cyanocyclopentadienide was isolated and characterised in the form of a potassium or tetraalkylammonium salt. Webster obtained in this way the complete series of cyanocyclopentadienides [41].

The ratio of the $\alpha\beta$-isomer to the $\alpha\gamma$-isomer in dicyano-products is approximately 6 : 1 and in tricyano-products the ratio of the $\alpha\beta\gamma$-isomer to the $\alpha\beta\delta$-isomer is 2 : 1, i.e. the selectivity of the position subjected to electrophilic attack in the substitution of cyano-groups in the cyclopentadienide anion corresponds to the selectivity in its methylation:



It is noteworthy that this method of synthesis of polycyanocyclopentadienides is much simpler than the method based on the cyclisation reaction. As an example, Scheme 1 presents a fairly complex method for the synthesis of the tetracyanocyclopentadienide ion [42,43]:

Scheme 1

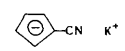
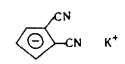
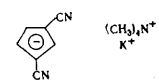
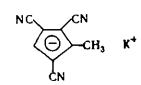
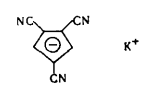
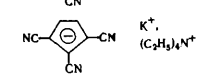
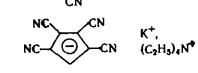
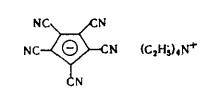
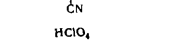


The stability of the resulting cyano-derivatives of the cyclopentadienide ion increases with the number of cyano-groups, as can be seen from the pK_a values for the corresponding conjugate acids (Table 1).

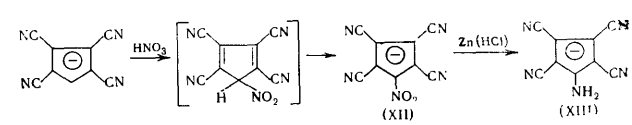
Table 1 shows that tricyanocyclopentadiene is a stronger acid than perchloric acid. The pentacyanocyclopentadienide ion is even more stable. For example, its potassium salt may be heated in air to 400°C without decomposition. The conjugate acid of this anion is very strong: pK_a(in CH_3CN) < -2, for comparison, we have for sulphuric acid pK_a(in CH_3CN) = 7.25. This anion is not protonated even by an acid as strong as perchloric in acetonitrile (spectrophotometric measurements). Probably the pentacyanocyclopentadienide ion has a very strong conjugate acid not only because of the pronounced electron-accepting properties of the five CN groups but also because it has pentagonal symmetry with a uniform delocalisation of the charge in each C–CN group.

It is noteworthy that the pentacyanocyclopentadienide ion and the very stable penta(methoxycarbonyl)cyclopentadienide [44], dicyanodi(ethoxycarbonyl)cyclopentadienide, and tetracyanocyclopentadienide ions [30] do not form ferrocenes on treatment with $FeCl_2$ in consequence of the delocalisation of the negative charge over the electron-accepting substituents. The derivatives obtained proved to be iron(II) salts. The iron(II) tetracyanocyclopentadienide salts are involatile and extremely sensitive to the action of air. These properties indicate an ionic and not a π-complex state of divalent iron.

Table 1. pK_a values for cyanocyclopentadienes in water and acetonitrile [41].

№	Conjugate base	pK_a (in water)	pK_a (in CH_3CN)	pK_a (calc.)
1		15 [2]	—	—
2		9.78	—	—
3		2.52	—	—
4		1.11	10.17 10.17	1.1
5		—	3.40	−5.7
6		—	3.0	−6.1
7		—	1.44 1.99	−7.8 −7.2
8		—	0.0 0.2	−9.1 −8.9
9		—	<−2	<−11
10		—	1.83	−7.3 −6.7

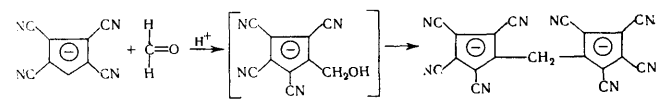
Acid electrophilic agents cannot be employed with unstable cyclopentadienide ions. However, in those cases where the basicity of the cyclopentadienide ion is greatly reduced by the introduction of electron-accepting groups, it is possible to employ also electrophilic agents which are strong acids. Thus concentrated nitric acid nitrates the tetracyanocyclopentadienide ion in 15 min (yield 67%) with formation of the tetracyanonitrocyclopentadienide ion (XII),



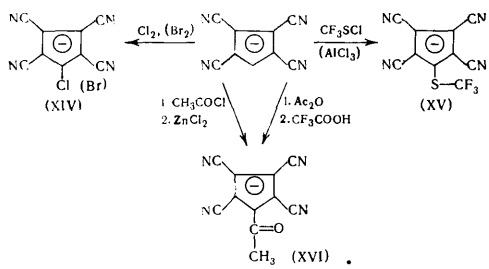
(XII) (XIII)

which could be reduced with zinc dust in hydrochloric acid to the already known [42] aminotetracyanocyclopentadienide

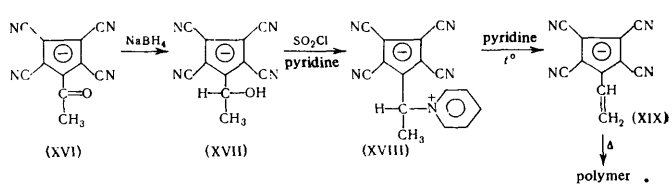
ion (XIII). The reactions of tetracyanocyclopentadienide with formaldehyde and acetaldehyde also take place in an acid medium [45]:



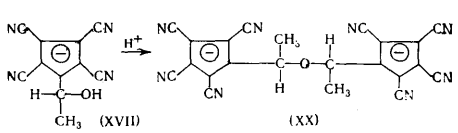
Friedrich [46] and Webster [45], who investigated electrophilic substitution in the tetracyanocyclopentadienide ion, believe that the reactivity of the latter resembles very closely that of anisole. Indeed, like anisole, the tetracyanocyclopentadienide ion reacts readily with halides, but for the reaction with trifluoromethanesulphenyl chloride, acetyl chloride, and acetic anhydride, catalysts of the Friedel-Crafts type or strong acids are required:



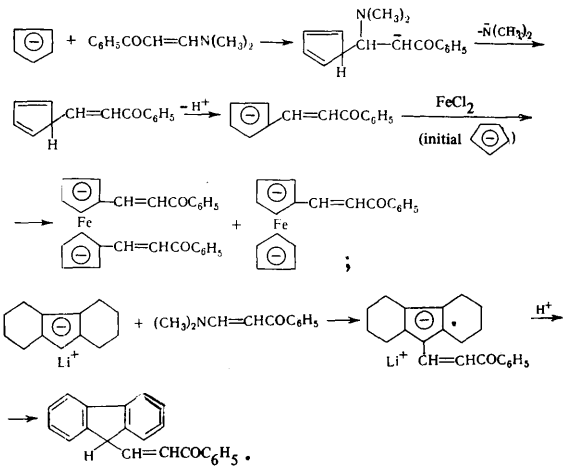
It is noteworthy that the high stability of polycyanocyclopentadienides made it possible to obtain a wide variety of their derivatives. Thus acetyltetracyanocyclopentadienide (XVI) was obtained for the synthesis of tetracyanovinylcyclopentadienide (XIX) according to the following mechanism:



Tetracyanovinylcyclopentadienide (XIX), which was isolated as the tetraethylammonium salt, readily polymerises at 135°C, giving a polymer soluble in acetonitrile. A suspension of the polymer in water may be used as an ion-exchange resin. It is interesting to note that the alcohol (XVII) formed as an intermediate in this synthesis reacts rapidly even with dilute acids to form the dianion of the ether (XX), probably via tetracyanomethylfulvene:

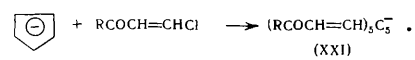


In contrast to polycyano-derivatives, monocyanocyclopentadienide ions, for example 9-cyanofluorene, readily react also with weak electrophilic agents such as alkyl halides [47-49]. By varying the activity of various electrophilic ketovinylating agents, Nesmeyanov and coworkers [50,51] achieved the mono- and poly-ketovinylation of cyclopentadienide ions. The reaction of sodium cyclopentadienide with β-dimethylaminovinyl phenyl ketone gave a monoketovinylated cyclopentadienide, which was identified in the form of ferrocene derivatives:



In this reaction lithium fluorenide gives, after treatment with acid, a high yield of monoketovinylated fluorene.

When a more active electrophilic agent (a β-chlorovinyl ketone) is employed, the reaction does not stop at the monoketovinylation stage but gives rise to coloured polyketovinylated ions, which according to spectroscopic data are most likely to have structure (XXI):



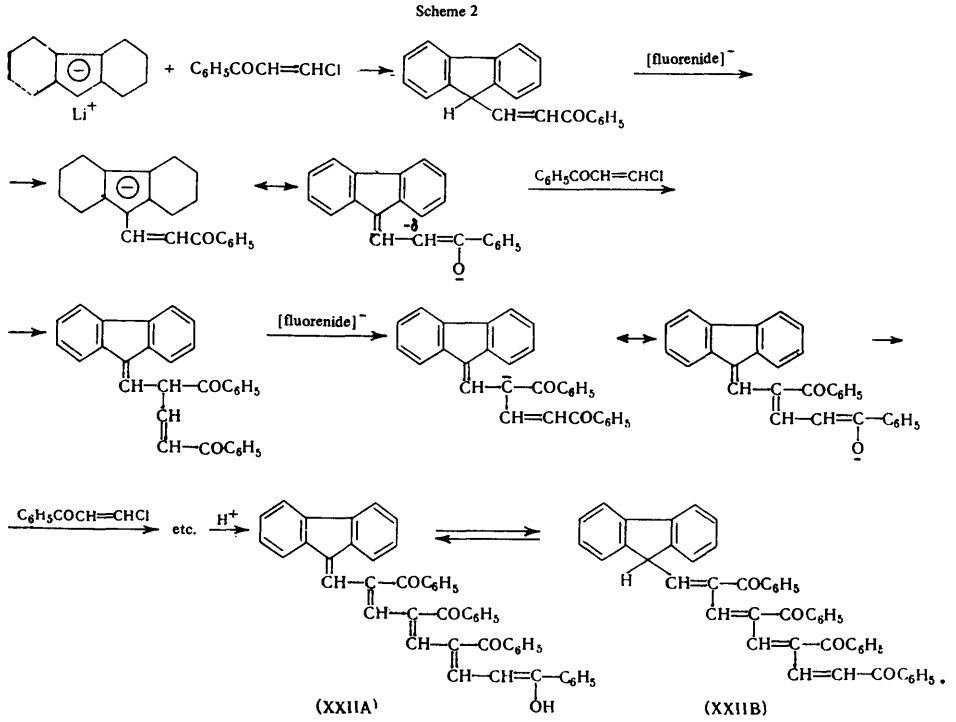
The introduction of five ketovinyl groups into the cyclopentadienide ion can be explained if one remembers that these groups have comparatively weak electron-accepting properties§ and are associated with a considerable steric effect, which lowers the delocalisation of the negative charge owing to the mutual displacement of these groups from the ring conjugation plane. The corresponding conjugate acids of these ions are comparable in strength to carbonic acid (for R = CH_3, pK_a = 7.2 in 50% aqueous alcohol and pK_a = 6.2 in water, while for R = C_6H_5, pK_a = 7.7 in 80% alcohol). However, such delocalisation of the negative charge and possibly also the appreciable steric hindrance proved to be the reason for the inability of the pentaketovinylated ions to form the corresponding ferrocenes on treatment of their sodium salts with iron(II) chloride.

The highly specific behaviour of these ketovinylating agents (RCOCH = CHCl) was noted in relation to lithium fluorenide, which has only one unsubstituted position in the five-membered ring. Whereas with a β-aminovinyl ketone (see above) a monoketovinylated ion was obtained, the reaction with β-chlorovinyl phenyl ketone yielded, after hydrolysis, an orange-red cryptocrystalline tetraketovinylated product, the structure of which has one of two tautomeric forms (XXII, A) or (XXII, B) (Scheme 2) according to molecular weight determinations (mass-spectrometric analysis), spectroscopic characteristics, and chemical reaction data:

---

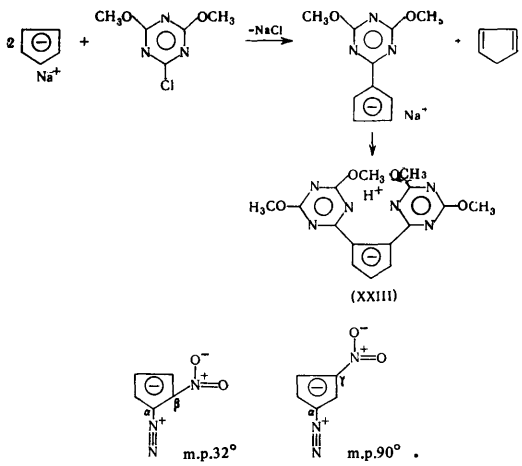
§If one remembers that the transmission coefficient of the *trans*-vinylene group [52] is about 0.5, the electron-accepting properties of the ketovinyl group are seen to be approximately twice as weak as those of the corresponding acyl groups.

Scheme 2

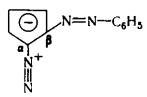


The reaction with 2-chloro-4,6-dimethoxy-*s*-trazine, which leads to the disubstituted product (XXIII),[53] should also be included among the electrophilic substitution reactions of cyclopentadienide ions.

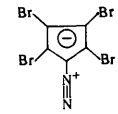
Ylides too are capable of electrophilic substitution reactions. Thus diazocyclopentadiene undergoes electrophilic substitution without the disruption of the ylide π-electron system, attack at the β-position predominating over attack at the γ-position[54]. In the nitration of diazocyclopentadiene the β-substituted product predominates over the γ-substituted product by a factor of 2:



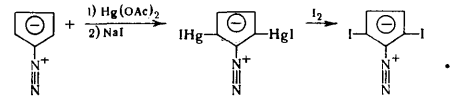
The reaction of phenyldiazonium tetrafluoroborate with diazocyclopentadiene also gives a product substituted in the β-position:



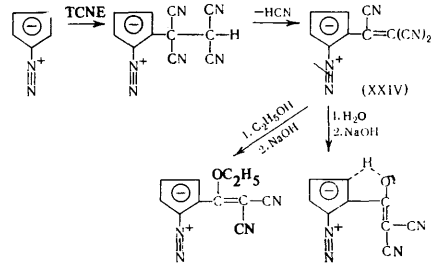
whereas bromination gives tetrabromodiazocyclopentadiene:



On mercuration, diazocyclopentadiene is converted into a very unstable 2,5-bis(iodomercuri)-derivative, which is readily converted into 2,5-di-iododiazocyclopentadiene:

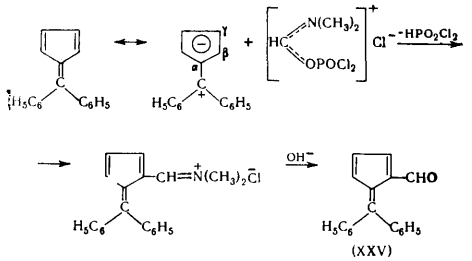


On reaction with tetracyanoethylene, diazocyclopentadiene forms an unstable acid, which easily loses HCN with formation of compound (XXIV), but the Diels–Alder reaction does not occur. Compound (XXIV) undergoes hydrolysis and ethanolysis typical for tricyanoethylenes[55,56]:



Electrophilic substitution in fulvenes has been little investigated. However, fulvenes are capable of electrophilic substitution like other non-benzenoid aromatic systems. Thus 6,6-diphenylfulvene (XXV) is readily formylated with a high yield on treatment with the

Vilsmeier complex[57]. In all the cases investigated, it was found that electrophilic attack on compound (XXVI) takes place at the β-carbon atom[58]:

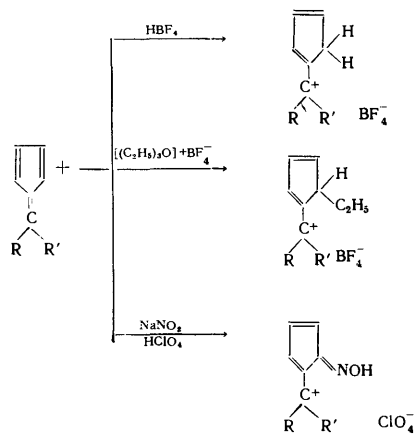


(XXV)

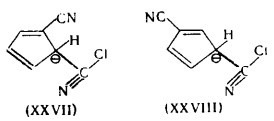
6,6-Diphenyl and 6,6-dimethyl-fulvenes are protonated, alkylated, and nitrosated at −80°C giving the corresponding cyclopentadienes, which are stable only at −80°C[59] (see below).

---oOo---

Thus electrophilic attack on all the cyclopentadienide ions investigated, containing both electron-accepting and electron-donating groups, is directed to the β-position. However, whereas in the presence of electron-donating groups substitution in the β-position could be explained on the basis of the distribution of electron density in the ring, with electron-accepting substituents an enhanced reactivity in the γ-position might have been expected.

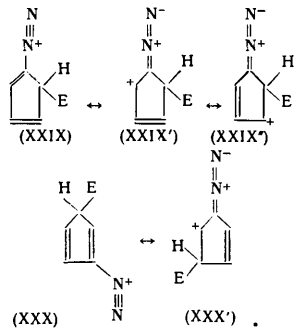


Therefore Webster[41] explains the higher content of the isomer with the CN group in the β-position in the reaction mixture obtained on substituting cyano-groups in the cyclopentadiene ion by the formation of a more stable transition state (XXVII), in consequence of the conjugation of the CN group with a diene system, compared with the transition state (XXVIII) in γ-substitution (a cross-conjugated system):



(XXVII) (XXVIII)

Cram and Partos[54], who studied electrophilic substitution in diazocyclopentadiene, explain their results similarly. They believe that the transition state in β-substitution is more stable, since the cation (XXIX) formed can be represented by three main contributions to the resonance hybrid [(XXIX) ⟷ (XXIX′)↕(XXIX″)], whereas the cross-conjugated cation (XXX) corresponding to γ-substitution has only two contributions [(XXX) and (XXX′)]:



(XXIX) (XXIX′) (XXIX″)

(XXX) (XXX′)

Table 2. Localisation energies (−β).

Model	2-Position	3-Position
	1.149	1.356
	1.685	1.734

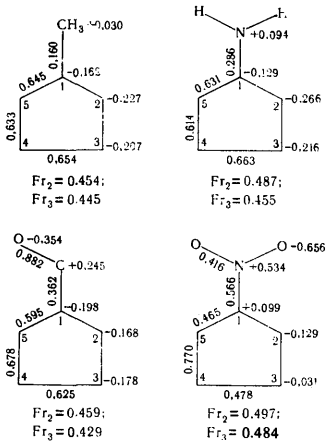


Figure 2. Molecular diagrams for cyclopentadienide ions containing electron-donating and electron-accepting substituents. The numerals against the carbon atoms denote the π-electronic charge and the numerals above the bonds denote the bond order. Fr = free valence index.

A general explanation covering cyclopentadienide ions with electron-donating and electron-accepting substituents is provided by the molecular orbital method. Indeed these results agree with the calculated (by the molecular orbital method) localisation energies (they usually vary in parallel with the free valence index) for monosubstituted cyclopentadienide radicals (Table 2).[60]

The authors note that the results of the calculation should be essentially proved also for the cyclopentadienide ions.

Calculations of the molecular diagrams presented below (Fig. 2) show that the higher reactivity of the β-position in relation to electrophilic substitution in derivatives with electron-donating substituents (CH_3 and NH_2 groups) is indicated both by the π-electronic charge and the free valence index. In the case of electron-accepting substituents, the free valence index again shows the β-position to be more reactive. Calculation of the π-electron density in terms of the Hückel approximation gives a less clear picture. In the presence of an electron acceptor as powerful as the NO_2 group, the β-position is found to have the highest π-electron density. The apparently unusual distribution of electron density under the influence of an electron-accepting substituent is associated with the non-alternant structure of the cyclopentadienyl ring. In the case of the carbonyl group the β-position has a somewhat lower electron density but only slightly so. Evidently calculation taking into account interelectronic interactions would suggest the opposite behaviour also in the presence of the carbonyl group (see the analogous case discussed by Bochvar et al. [61]). Thus the higher reactivity of the β-position regardless of the type of substituent is fully consistent with the π-electron reactivity indices of the substituted non-alternant cyclopentadienyl ring.

It is noteworthy that the electrophilic attack on the β-position observed in the case of fulvenes is also consistent with the calculated distribution of electron density and localisation energy [62,63].

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Conversions of Chlorine-containing Aliphatic Compounds in the Presence of Coordination-unsaturated Metals

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Conversions of aliphatic chlorine-containing compounds (chloroalkenes, chloroalkanes, and derivatives of chloro-substituted carboxylic acids) occur under the action of aprotic acids. Chloroethylenes are polymerised by a cationic mechanism with the formation of oligomeric and polymeric products. The principal reaction of chloroalkanes and chlorocycloalkanes in the presence of salts of coordination-unsaturated metals is dehydrochlorination, which proceeds either intramolecularly or intermolecularly with the formation of polymers with conjugated double bonds. For polychloro-containing compounds, in addition to the dehydrochlorinations, elimination of chlorine occurs. Perchloroalkanes (from C_3 and higher) in the presence of aprotic acids also undergo degradation with breaking of the carbon-carbon bond. There is a bibliography of 353 references.

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I. INTRODUCTION

Chlorine-containing organic compounds are readily available and extremely reactive. They are starting materials for making various organic compounds of practical importance. Many reactions with chlorine-containing products take place in the presence of Friedel–Crafts catalysts. They include the alkylation and acylation of aromatic compounds, addition to alkenes, and replacement of chlorine atoms by other halogens and functional groups and have been discussed in monographs[1-3] and reviews[4-7].

It was noted long ago that reactions involving chlorine-containing compounds in which Lewis acids are used as catalysts are accompanied by conversions of the chlorine-containing reagent itself, which reduces the yield of the main product and contaminates it with various impurities. A characteristic example of such changes is the decarbonylation, in the presence of aluminium chloride, of acyl chlorides with a branch in the α position. Addition of alkyl halides, acyl chlorides, and other compounds to chloroalkenes is accompanied by conversions of each of the reagents separately. In addition to the formation of polyconjugated polymers ("tar"), degradation is observed[4].

Some chloroalkanes and chloroalkenes are widely employed as extractants in heavy organic synthesis (for example, trichloroethylene in the production of ϵ-caprolactam) and in the metallurgical industry for degreasing metal surfaces. Sometimes contact between the solvents used and salts of coordination-unsaturated metals is possible, which brings about the undesirable conversions of the chloroalkanes and chloroalkenes, leading to contamination of the product being extracted and of the solvent.

The reactions of chlorinated hydrocarbons in the presence of Friedel–Crafts catalyst are of independent importance. Thus the dehydrochlorination of chloroalkanes is used for obtaining industrial monomers (vinyl chloride and vinylidene chloride) and trichloroethylene.

The use of chlorine-containing compounds as solvents in the cationic polymerisation of alkenes is well known[8,9]. The part played by the solvent in this is enormous, since the degree of polymerisation of the monomer, the molecular weight, and sometimes also the stereoregularity of the polymer obtained depend partly on it. The effect of the solvent on the course of the polymerisation and the properties of the polymer have recently been linked with the fact that the solvent reacts with the catalyst to form reactive species which participate directly in the polymerisation of the monomer.

Some chlorine-containing compounds can be regarded as models of individual units of such chlorine-containing polymers as poly(vinyl chloride), poly(vinylidene dichloride), chlorinated poly(vinyl chloride), chlorinated polyethylene, etc. Therefore information about the conversions of these compounds in the presence of aprotic acids can be used in studying the mechanism of degradation and analogous conversions of chlorine-containing polymers.

Unlike reactions of organochlorine compounds with other reagents, the conversions of certain solely aliphatic chlorine-containing compounds in the presence of aprotic acids have not been reviewed. The present review is an attempt to survey the available published information on the conversions of chloroalkanes and chloroalkenes in the presence of Lewis acids. This review does not consider the conversions of chlorine-containing aromatic compounds, since the work on this subject has been covered adequately in a monograph[2].

II. CHLOROMETHANES AND THEIR DERIVATIVES

1. CHLOROMETHANES

Chloromethanes are extremely stable compounds and in the absence of atmospheric oxygen they can be stored and distilled without decomposition. The ability of chloromethanes to withstand high temperatures depends on the number of chlorine atoms in them and drops from methyl chloride to chloroform, owing to the decrease in the energy for breaking the C–Cl bond (Table 1). In addition, to high dielectric constants, especially for methyl chloride and methylene dichloride, show that under certain conditions these compounds can be extremely reactive. With such electrophilic compounds as the halides of coordination-unsaturated metals, the chloromethanes form, even at low temperatures (−80, −20°C), stable complexes of the type

$CH_3Cl.AlBr_3$ or $CH_3Cl.Al_2Br_6$, [13,14] in which there is an exchange of halogen atoms between chloromethane and the complex-forming substance [15-17]. With the aid of this reaction, which is effected through a transitional six-membered transition complex [17], carbon tetrabromide can be obtained in high yield from carbon tetrachloride and $AlBr_3$. [18]

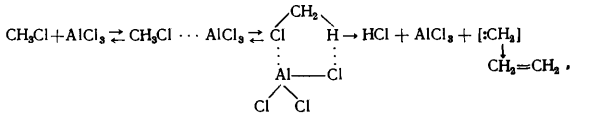
At elevated temperatures more extensive conversions of chloromethanes take place.

Table 1. Characteristics of chloromethanes [10-12].

Chloromethane	Decomposition temp., °C	Energy for breaking the C-Cl bond at 400-500°C, kcal mole^{-1}	Energy for breaking the C-H bond at 400-500°C, kcal mole^{-1}	Dielectric constant at 20°C	Distance between chlorine atoms, Å
CH_3Cl	1400	80.5	98.0	12.61	—
CH_2Cl_2	720	73.4	95.0	8.40	3.16
$CHCl_3$	290	66.5	90.2	4.84	3.04
CCl_4	400	76.0	--	2.24	2.58

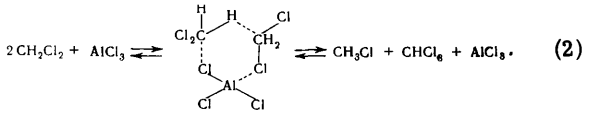
Methyl chloride. Under the action of $AlCl_3$ at 20°C methyl chloride is converted into hydrogen chloride and ethylene [19]. It could be expected that an intermediate product in the conversion of methyl chloride into ethylene would be ethyl chloride, formed as a result of the condensation of two molecules of methyl chloride. However, the main products of the reaction of ethyl chloride with $AlCl_3$ are polymers [20] (see p. 262) and among the products of the reaction of methyl chloride with $AlCl_3$ neither ethyl chloride nor a polymer were observed. It is also improbable that the conversion of methyl chloride into ethylene proceeds by an ionic mechanism [21,22].

It is assumed [23] that this process is carbenoid in nature and proceeds by intermediate formation of a five-membered transition complex (scheme 1):



(1)

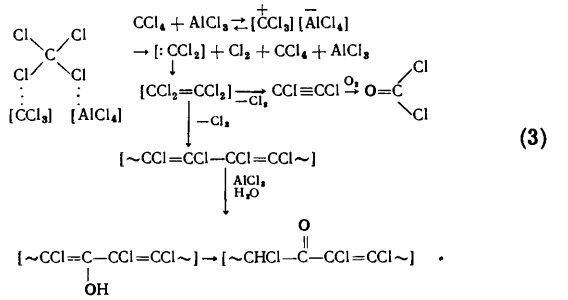
When a mixture of methylene chloride and $AlCl_3$ is heated to 40°C, a disproportionation (little known for chloroalkanes) takes place, as a result of which methyl chloride and chloroform are formed [19] (scheme 2):



(2)

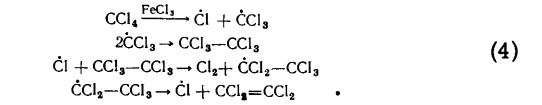
Furthermore, hydrogen chloride, *trans*-1,2-dichloroethylene, and a polymer of composition $(C_2H_5Cl)_n$ were identified in the reaction products. The formation of 1,2-dichloroethylene from methylene dichloride probably takes place just like the formation of ethylene from methyl chloride, by α-elimination of hydrogen chloride. The polymer $(C_5H_5Cl)_n$ had the same composition and properties as the polymer formed on heating chloroform with the same catalyst to 60°C. Evidently when methylene dichloride is heated with $AlCl_3$, the chloroform which is formed in the disproportionation of methylene dichloride undergoes polycondensation. The polycondensation of chloroform [19] in this instance can be based solely on intermolecular dechlorination. This is shown by the carbon : hydrogen ratio in the polymer, which remains equal to 1 : 1, that is, the same as in the initial chloroform.

In contrast with the other chloromethanes carbon tetrachloride in the presence of $AlCl_3$ undergoes conversions only on heating under severe conditions, for example, at 200°C. [19] Here the main process is the ionisation of the carbon tetrachloride with the formation of the rather stable carbonium ion $\dot{C}Cl_3$. [21,22] The appearance of the carbonium ion is shown by the reaction mass being pink, by absorption in the 530 mμm region, and by the quantitative formation of chloroform in the reaction of carbon tetrachloride with n-hexane in the presence of $AlCl_3$. In addition to ionisation, slight conversion of carbon tetrachloride into dichloroacetylene, carbonyl chloride, and a polymeric product of composition $(C_6H_3Cl_2O_3)_n$ is observed [19]. Dichlorocarbene is evidently an intermediate product of this reaction (scheme 3). The possible formation of dichlorocarbene under similar conditions has already been reported [24]. Support for scheme 3 is provided by the fact that when heated with $AlCl_3$ tetrachloroethylene actually undergoes intramolecular and intermolecular dechlorination with the formation of dichloroacetylene and a polymer (cf. p. 261). The presence of hydrogen and oxygen in this polymer is explained by its interaction with water in the presence of $AlCl_3$: [19]



(3)

The conversions of chloromethanes in the presence of aprotic acids in the gas phase have been little studied. The results published on this subject relate mainly to CCl_4. On passing CCl_4 vapour over iron, zinc, copper, and other metal chlorides at 200–300°C, chlorine, hexachloroethane, and tetrachloroethylene are formed [25-27], that is, the same products as are formed from CCl_4 in high-temperature (700–800°C) pyrolysis [28-32] in the absence of catalysts. According to some results [25-27] the catalytic decomposition of CCl_4 into chlorine, hexachloroethane, and tetrachloroethylene proceeds by a radical mechanism (scheme 4):



(4)

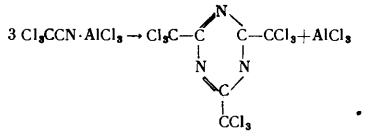
2. SUBSTITUTED CHLOROMETHANES

The replacement of chlorine atoms in chloromethanes by other groups alters the reactivity of the chlorine atoms in chloromethanes. The substituents at which the electronic density is greatest react with aprotonic acids.

Chlorofluoromethanes greatly surpass chloromethanes as regards reactivity in the presence of Lewis acids [33-45]. Under the action of $AlCl_3$ or $AlBr_3$ fluorine-containing chloromethanes readily disproportionate [36-43].

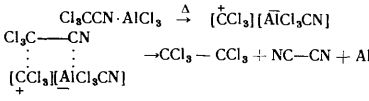
Thus fluoroform is obtained in quantitative yield from dichloro(fluoro)methane at 50°C, [36] whereas under these conditions the disproportionation of chloromethanes is very slow[19].

The introduction of a nitrile group into chloromethanes increases their reactivity even more. The reaction of chloroacetonitriles with aprotic acids begins with complex formation by the nitrile group[2,46,47]. A series of stable complexes of the type $CCl_3CN.MX$, $2CCl_3CN.MX$, and $CCl_2CN.2MX$ is formed. When the complexes are heated to 100°C, trimerisation of the trichloroacetonitrile takes place with the formation of 2,4,6-tris(trichloromethyl)-1,3,5-triazine[46] (scheme 5):



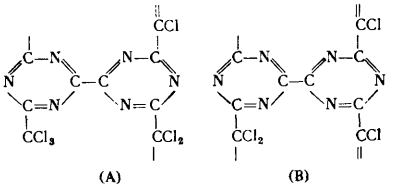
(5)

The same triazine is also obtained by saturation of trichloroacetonitrile with hydrogen chloride in the presence of catalytic amounts of $AlCl_3$ or $AlBr_3$.[48-51] When the complexes of trichloroacetonitrile with $AlCl_3$ are heated to 140–150°C, heterolytic breaking of the carbon–carbon bond of the nitrile occurs, which leads to the formation of hexachloroethane and dicyanogen. The suggested scheme of reaction (6) is confirmed by the formation of chlorotriphenylmethane when the complex $2Cl_3CCN.AlCl_3$ is boiled with benzene. If there were homolytic breaking of the C–C bond the trichloromethyl radical, which is inert in relation to benzene, would be formed[52]:



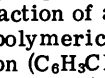
(6)

In addition to hexachloroethane and dicyanogen, when complexes of trichloroacetonitrile with $AlCl_3$ are heated, polymeric products of composition $(C_9Cl_6N_6)_n$ and $(C_9Cl_4N_6)_n$ are formed, which contain units of composition (A) and (B), were obtained:

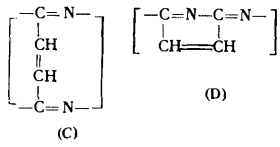


(A) (B)

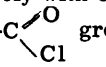
It has been shown[46] that the formation of these polymers takes place not by the polymerisation of triazine with ring opening[53-55], but by the polymerisation of trichloroacetonitrile and of dicyanogen at the nitrile groups with subsequent dechlorination of the CCl_3 side-groups.

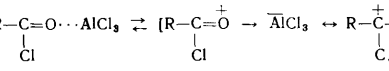
A similar picture is observed in the reaction of dichloroacetonitrile[56] with $AlCl_3$. By heating the complex $2CHCl_2CN.AlCl_3$ to 70°C, 2,4,6-tris(dichloromethyl)triazine can be obtained, which is also formed on prolonged saturation of the nitrile with hydrogen chloride[57]. At temperatures above 80°C the $CHCl_2$ side-groups of the triazine undergo dechlorination under the action of aluminium chloride, with the formation of a polymeric product with conjugated double bonds of composition $(C_6H_3Cl_3N_3)_n$, consisting of triazine rings connected by  bridges[56].

Unlike tri- and di-chloroacetonitriles, monochloroacetonitrile does not trimerise to a triazine in the presence of small quantities of aprotic acids[58]. When the complex $2CH_3ClCN.AlCl_3$ is heated above 200°C, as for other unsaturated nitriles[59-64] polymerisation of the nitrile at the nitrile groups takes place with formation of a chain of conjugated –C=N– bonds. Simultaneously with the polymerisation, dehydrochlorination of the chloromethyl side-groups takes place, as a result of which units of types (C) and (D) arise in the polymer.



(C) (D)

Chloroacetyl chlorides can be regarded as chloromethanes in which the central carbon atom is connected, not solely with chlorine and hydrogen atoms, but also with the  group. As for other acyl chlorides[65,66], the reaction of these compounds with salts probably begins with the formation of complexes of type .$AlCl_3$ or .Al_2Cl_6, in which exchange of halogen atoms between the acyl chloride and the salt can take place[67]. There are differences of opinion concerning the reaction centre in acid chlorides in the formation of complexes. Some consider[6,68-70] that the active centre in organic acyl chlorides is the oxygen of the carbonyl group and with aprotic acids complexes of the following type are formed:



However, it has been shown[71] by infrared spectroscopy that the chlorine in the acyl chloride is subjected to electrophilic attack by the aluminium chloride, which leads to the formation of an ion-pair $[R\overset{+}{C}{=}O][\overline{Al}Cl_4]$. Such a viewpoint is maintained by Palmer and McVie[72]. It has recently been shown[73] spectroscopically that both types of complex formation occur and the predominance of one over the other depends primarily on the structure of the initial acyl chloride. Electron-donating substituents in the acid residue of the acyl chloride increase the electron density in the –COCl group, which facilitates reaction with aprotic acids at the oxygen atom. Electron-withdrawing substituents depress the nucleophilic properties of the oxygen atom and therefore the complex with the catalyst is formed preferentially at the chlorine atom. This evidently relates to a compound such as trichloroacetyl chloride.

When the complexes of acyl chlorides and aprotic acids are heated, they decompose with the liberation of carbon monoxide and the formation, usually, of the corresponding alkyl chlorides[74-81]. Electron-donating substituents in the acid residue accelerate the elimination of carbon monoxide, and electron-withdrawing substituents retard it[82-84]. In this connection the decarbonylation of the acid chlorides in the last instance is carried out at high temperatures and in the presence of large amounts of catalyst. According to these results, when trichloroacetyl chloride is heated to 100°C in the presence of aluminium chloride decomposition of the acid chloride by scheme (7) to carbon

monoxide and carbon tetrachloride takes place[85,86]. In addition to the compounds mentioned, conversion products of CCl_4 (see scheme 3) are also formed—dichloroacetylene and a polymer[86]:

$$CCl_3C(=O)\cdots AlCl_3 \xrightarrow{\Delta} [CCl_3\overset{+}{C}{=}O][\overline{A}lCl_4] \rightarrow CO + [\overset{+}{C}Cl_3][\overline{A}lCl_4] \quad (7)$$

$$[\overset{+}{C}Cl_3][AlCl_4] \rightarrow CCl_4 + AlCl_3 \quad .$$

When dichloroacetyl chloride is heated with aluminium chloride in chloroform solution it also decomposes with release of carbon monoxide[87]. When a mixture of chloroacetyl chloride and aluminium chloride is heated there is an intensive evolution of carbon monoxide and also of hydrogen chloride and chloroacetylene and the formation of a polymeric product with conjugated double bonds and a carbon : hydrogen : chlorine ratio of 4 : 4 : 1.[86] The decomposition of chloroacetyl chloride probably takes place just like the decomposition of trichloroacetyl chloride (scheme 7), that is, through the intermediate production of an acylcation, reaction of which is effected by loss of carbon monoxide[88]. Here the formation of hydrogen chloride and chloroacetylene is due to secondary conversions of methylene dichloride.

Carbonyl chloride with aprotic acids gives stable complexes[69,89] in which exchange of halogen atoms takes place[67]. In the gas phase at 300–400°C[90,91] under the action of aprotic acids decomposition of carbonyl chloride takes place with the formation of carbon monoxide and carbon tetrachloride.

In esters of chloroacetic acids, as in the acyl chlorides of these acids, reaction with Friedel–Crafts catalyst occurs first at the ester group. At low (−20°; +30°C) temperatures, esters of trichloroacetic acid and $TiCl_4$ form unstable complexes of composition $2TiCl_4.CCl_3COOR$, $TiCl_4.CCl_3COOR$, and $TiCl_4.2CCl_3.COOR$.[92,93] The lower stability of these complexes in comparison with esters of unsubstituted aliphatic acids[94–100] is due to the increased electron-withdrawing properties of the CCl_3 group. Spectroscopic investigations in recent years have shown convincingly that complex formation by esters with the salts of coordination-unsaturated metals is effected at the carbonyl oxygen of the ester group[101–106].

Careful heating of the complexes of esters with aprotic acids caused them to melt and dissociate into the initial components. Above the melting points of the complexes and also in the presence of large quantities of aprotic acids some esters decompose readily with formation of alkyl halides and salts of organic acids[107–110]. An analogous picture is also observed on heating a mixture of methyl trichloroacetate and aluminium chloride, taken in a ratio between 1 : 1 and 3 : 1. Methyl chloride and bis(trichloroacetate)–aluminium chloride were thus obtained[111]. When the reaction was carried out under more severe conditions (higher temperature, increase in the excess of $AlCl_3$) tetrachloroethylene appeared in the reaction products in addition to the compounds listed above[111]. The formation of these compounds can be explained with the aid of schemes (8) and (9), according to which complexes (A) and (B) arise as intermediate products of the reaction; in the latter there is exchange of a chlorine atom of aluminium chloride for the acid residue of the ester:

$$CCl_3{-}C(=O\cdots AlCl_3){-}OCH_3 \rightleftarrows CCl_3{-}C(=O){-}OCH_3\ (AlCl_3) \quad (8)$$

(A) (B)

$$CCl_3C(=O)\cdots O(AlCl_2)\cdots Cl{-}CH_3 \xrightarrow{\Delta} CCl_3C(=O)OAlCl_2 + CH_3Cl$$

$$[CCl_3^-] \xrightarrow{-Cl^-} [:CCl_2] \rightarrow CCl_2{=}CCl_2 \quad . \quad (9)$$

The aluminium salt of trichloroacetic acid, like the other salts of this acid[112,113], is further decarboxylated with the formation of the carbanion CCl_3^-, which is converted into dichlorocarbene and then into tetrachloroethylene. The intermediate formation of the $\overline{C}Cl_3$ anion is shown by the fact that when the reaction mass is treated with water chloroform is observed in the products[111].

In the presence of salts of coordination-unsaturated metals alkyl chloroformates readily decompose with liberation of carbon dioxide and an alkyl halide[114,115].

The formation of aluminium salts and chloroalkanes in the reaction of esters with $AlCl_3$ enables the effect of the structure of the esters on their ability to acylate and alkylate aromatic compounds after Friedel–Crafts to be explained. Esters of aliphatic alcohols and organic acids which contain electron-withdrawing substituents (chloroacetic, trichloroacetic, $\alpha\beta$-dichloropropionic, benzoic, oxalic, etc.) only alkylate benzene, since the aluminium salts of these acids exhibit weak acylating properties[111]. Conversely, esters of aliphatic alcohols and unsubstituted aliphatic acids give with benzene both alkylation products and acylation products, since the aluminium salts then formed exhibit high acylating properties[108,110,111,116,117]. And, finally, esters containing electron-withdrawing substituents simultaneously in both the acid and the alcohol radicals do not enter into any reaction with benzene in the presence of Friedel–Crafts catalysts. In this instance the ester probably does not decompose into salt and alkyl halide.

Phenyl-substituted chloromethanes are distinguished by high reactivity. The presence of phenyl groups creates increased electron density at the chlorine atom, as a result of which its mobility increases sharply. The polycondensation of benzyl chloride in the presence of aprotic acids is undoubtedly of interest[118–132]. This reaction was described in detail in a recently published review[133] and allows thermally stable polymers to be obtained from saturated chlorine-containing compounds.

The chlorine in chlorotriphenylmethane is even more labile than that in benzyl chloride. Under the action of Friedel–Crafts catalysts chlorotriphenylmethane dissociates readily with the formation of a stable carbonium ion[134–136]. Here the degree of ionisation of chlorotriphenylmethane depends considerably on the nature of the catalyst and the solvent. In their ability to eliminate a chlorine ion from chlorotriphenylmethane the catalysts are arranged in the following series: $SbCl_5 \simeq FeCl_3 > GaCl_3 > SnCl_4 > BCl_3 > ZnCl_2 > TiCl_4 > SbCl_3 > AlCl_3 > PCl_5$.

III. CHLOROALKENES

1. CHLOROETHYLENES

Chloroethylenes which contain one or two chlorine atoms (vinyl chloride, vinylidene dichloride, and 1,2-dichloroethylene) are stable at high temperatures in the absence of atmospheric oxygen[137–141]. Vinyl chloride does not lose hydrogen chloride even when treated with bases[139].

The extremely high stability of these chloroethylenes, owing to the low mobility of their chlorine atoms, is used for the preparation of vinyl chloride, vinylidene chloride, and 1,2-dichloroethylene by pyrolysis of the corresponding chloroethanes[137,140]. The low lability of the chlorine atoms in these chloroethylenes is explained by the presence of conjugation between the unshared electron pairs of the chlorine atoms and the double bond:

$$CH_2{=}CCl_2 \leftarrow \overset{+}{C}H_2{-}CCl{=}\overset{+}{C}l.$$

Owing to this, the distance between the carbon and chlorine is shortened and becomes less (Table 2) than in saturated chlorinated hydrocarbons (for example, it is 1.77 Å in ethyl chloride).

Trichloroethylene and tetrachloroethylene, unlike the mono- and di-chloroethylenes, are unstable during storage and when heated. To suppress dehydrochlorination and other side-reactions, tri- and per-chloroethylenes were distilled in the presence of stabilisers[142-146]—hydrazones[144,145], epoxy-compounds[146], etc. The diminished thermal stability of trichloroethylene and tetrachloroethylene is due to the greater lability of the chlorine atoms in them. This is shown by the lower ionisation potentials and the increase in the C–Cl bond length in these compounds (Table 2).

Table 2. Characteristics of chloroethylenes[10,147,148].

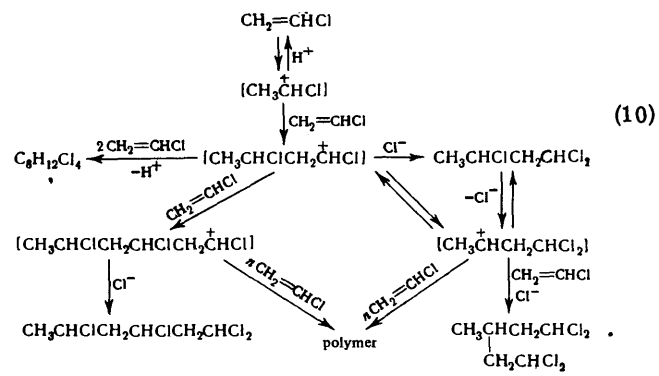
Chloroethylene	Ionisation potential, eV	C–Cl distance, Å	Dipole moment in benzene, D
$CH_2{=}CHCl$	9.99	1.69	1.44
$CH_2{=}CCl_2$	9.79	1.69	1.40
cis-CHCl-CHCl	9.66	1.67	1.85
trans-CHCl=CHCl	9.96	1.69	0.0
$CHCl{=}CCl_2$	8.80	1.82	0.94
$CCl_2{=}CCl_2$	9.50	1.82	0.0

The behaviour of chloroethylenes in the presence of aprotic acids is also different.

From the nature of the changes which chloroethylenes undergo in the presence of Lewis acids they can be divided into two groups. The first group of chloroethylenes (vinyl chloride, vinylidene chloride, and both isomers of 1,2-dichloroethylene) has a tendency to polymerise by a cationic mechanism in the presence of aprotic acids[138,139,149-156]. Trichloroethylene and tetrachloroethylene constitute a second group and are distinguished from the representatives of the first group by their undergoing autocondensation under the action of cationic catalysts.

a. Polymerisation of Chloroethylenes

Vinyl chloride is readily protonated in the presence of cationic catalysts ($AlCl_3$ or $TiCl_4$) owing to the moistness of the catalyst, with the formation of the reactive carbonium ion $CH_3\overset{+}{C}HCl$. This positively charged species, like other carbonium ions[159,160] initiates further polymerisation of vinyl chloride at –10°C[154-156] with the formation of oligomeric and polymeric products (scheme 10). The reaction of the $CH_3\overset{+}{C}HCl$ cation with a molecule of vinyl chloride leads to the formation of a new carbocation $CH_3CHClCH_2\overset{+}{C}HCl$, which is partly neutralised by the chlorine anion with the formation of trichlorobutane[154-158]. Furthermore, by successive addition of one or two molecules of vinyl chloride the dimeric cation is converted further into 1,1,3,5-tetrachlorohexane and tetrachloro-octene. Simultaneously, the cation $CH_3CHClCH_2\overset{+}{C}HCl$ isomerises into the cation $CH_3\overset{+}{C}HCH_2CHCl_2$. The latter reacts with vinyl chloride and is converted into 1,1,5,5-tetrachloro-3-methylpentane. As a result of further chain growth and secondary conversions of the oligomeric compounds with the vinyl chloride a low-molecular-weight polymer with a degree of polymerisation of ~ 30 is obtained, which consists of (–CH=CH–) and ($-\underset{\displaystyle CH_2CHCl_2}{\underset{|}{CH}}-CH_2-$) units in the ratio 1 : 1[154-156].



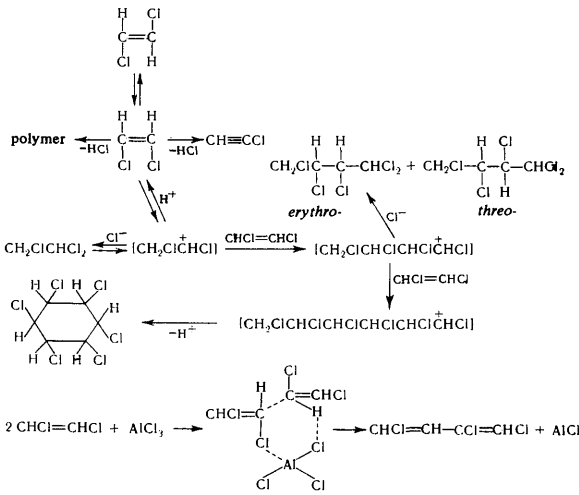
Raising the polymerisation temperature of vinyl chloride to 0°C or over accelerates the reaction, but simultaneously increases the rate of dehydrochlorination of the polymeric product formed. Therefore the polymer contains up to 80% vinylene units[154-156].

Owing to its asymmetric structure and comparatively large dipole moment (Table 2), *cis*-1,2-dichloroethylene is more reactive than the *trans*-isomer[147,161,162]. This is also true of reactions in the presence of aprotic acids. At room temperature under the influence of $AlCl_3$ both isomers of 1,2-dichloroethylene undergo only mutual interconversions into one another (scheme 11)[152]. The isomerisation of *trans*-1,2-dichloroethylene is effected at a greater rate than that of the *cis*-isomer[163,164].

The cationic polymerisation of 1,2-dichloroethylene is effected only at 50–70°C and is broken at the stage of formation of a dimeric compound (mixture of *erythro*- and *threo*-isomers of 1,1,2,3,4-pentachlorobutane)[152,155,156,165] and the trimer α-1,2,3,4,5,6-hexachlorocyclohexane[152,156]. Further polymerisation of 1,2-dichloroethylene does not take place, since the dimers give stable and unreactive complexes with the catalyst ($AlCl_3$) and the trimeric cation is cyclised (scheme 11). Furthermore, under these conditions under the influence of aluminium chloride pseudo-ionic processes of intramolecular and intermolecular dehydrochlorination of 1,2-dichloroethylene and its polymerisation products occur, as a result of which chloroacetylene and a polymeric product consisting of (–CH=CCl–) and ($\rangle C{=}CHCl$) units are formed[152].

Intermolecular dehydrochlorination of 1,2-dichloroethylene can be effected in the transition complex by

simultaneous electron transfer (scheme 12). The hydrogen chloride thereby liberated reacts with 1,2-dichloroethylene, which leads to the formation of 1,1,2-trichloroethane [152,166].

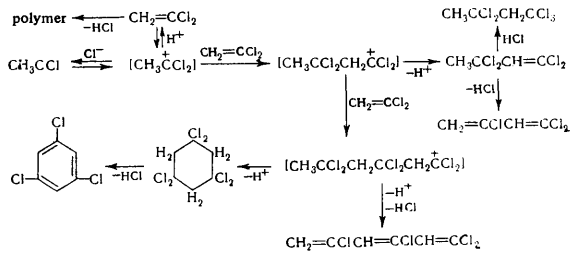


(11)

(12)

Vinylidene chloride at −50°C in the presence of $AlCl_3$ gives low-molecular-weight products of the polymerisation: the dimer [167] 1,1,3,3-tetrachlorobutene [150] and a cyclic trimer, 1,1,3,3,5,5-hexachlorocyclohexane [150]. On raising the temperature the polymerisation is accompanied by disproportionation of the 1,1,3,3-tetrachlorobutene to 1,1,1,3,3-tetrachlorobutene to 1,1,1,3,3-pentachlorobutane and 1,1,3-trichlorobutadiene (scheme 13), and also by dehydrochlorinations, as a result of which unsaturated compounds are formed: 1,1,3,5-tetrachlorohexatriene, 1,3,5-trichlorobenzene and a polymer with conjugated double bonds and with a composition close to $(CH_2Cl)_n$.

In the presence of $ZnCl_2$, which is a weaker complex-forming substance and cyclising agent than $AlCl_3$, vinylidene chloride is smoothly polymerised at 30°C with the production of poly(vinylidene chloride) [153]. This polymer is distinguished from the poly(vinylidene chloride obtained by radical polymerisation [168] by higher crystallinity [153].



(13)

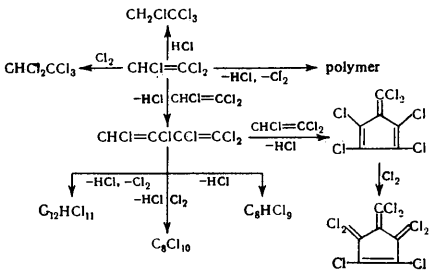
Hence the structure of chloroethylenes and the stability of the carbonium ions formed from them are the deciding factors in cationic polymerisation of these monomers. The chloroethylenes can be arranged according to their ability to polymerise in the following order [156]:

$$CH_2{=}CCl_2 > CH_2{=}CHCl > CHCl{=}CHCl\ [156].$$

It is noteworthy that in the case of vinyl chloride polymerisation in the presence of $AlCl_3$ leads to polymeric products, whereas with vinylidene chloride and 1,2-dichloroethylene the polymerisation is broken at the stage of cyclic trimer formation. Cyclisation of the trimeric cations is explained by the curvature of these cations in space and the possibility of a release of energy in the formation from them of uncharged six-membered rings [169].

b. Autocondensation of Chloroethylenes

For trichloroethylene the tendency to autocondensation is even greater than for 1,2-dichloroethylene (p. 260). In the presence of $AlCl_3$ trichloroethylene loses HCl even at −10°C. [170] As for 1,2-dichloroethylene, the autocondensation of trichloroethylene is probably effected by a pseudo-ionic mechanism and leads to the formation of oligomeric and polymeric products (scheme 14) [170,171]. Here the dimeric product [166,170–176] is a mixture of the *cis*- and *trans*-isomers of 1,1,2,3,4-pentachlorobutadiene [170,171].



(14)

The polycondensation of trichloroethylene and of the products of the oligomerisation to a polymeric product containing units of the −CCl=CCl− type and five-membered rings, proceeds both by dehydrochlorination and by dechlorination. The hydrogen chloride and chlorine thus liberated are partly consumed in the reaction with unsaturated compounds, which leads to the appearance among the reaction products of non-symmetric tetrachloroethane [170] and pentachloroethane [171].

On heating a mixture of tetrachloroethylene and aluminium chloride to 100–110°C, intermolecular and intramolecular dechlorination of tetrachloroethylene occur, with the formation of dichloroacetylene, hexachloroethane, and a polymeric product with conjugated double bonds [19], analogous in composition and properties to the polymer obtained from CCl_4 (cf. scheme 3).

Hence, autocondensation of chloroethylenes under the action of $AlCl_3$ takes place readily in those instances when the chlorine atoms in chloroethylenes (trichloroethylene and tetrachloroethylene) exhibit sufficient lability (cf. Table 2).

2. OTHER CHLOROALKENES

Chloroalkenes without chlorine atoms or with one or two chlorine atoms polymerise according to a cationic mechanism with the formation of oligomeric [177–180] and polymeric [181–183] products. Thus in the presence of $AlCl_3$ at 50°C allyl chloride gives di-, tri-, tetra-, and pentamers [180] which have the structure

$$CH_3CH(CH_2Cl)-[CH_2CH(CH_2Cl)-]_nCH{=}CHCH_2Cl.$$

On raising the temperature to 100–200°C the depth of the polymerisation of the allyl chloride is greatly increased [182,183]. However, simultaneously with this, dehydrochlorination of the polymerisation products takes

place, which leads to the production of a polymer containing unsaturated links of the type $-CH_2-\overset{}{\underset{}{C}}-$ type in $\overset{}{\underset{CH_2}{\|}}$ addition to allyl chloride units[183].

The polymerisation[181] of methyl-substituted allyl chloride—3-chloro-3-methylbut-1-ene—in the presence of $AlCl_3$ is accompanied by exchange of the chlorine atom and methyl group, which leads to the production of a polymer containing different units[181,184-186].

Polychlorine-containing alkenes with aprotic acids form stable, often coloured, complexes[4,187] in which exchange of halogen atoms between the chloroalkene and catalyst takes place[188-191]. The exchange by the halogens is used for obtaining chlorofluoroalkenes; exchange proceeds readily on heating chloroalkenes with fluorides of coordination-unsaturated metals[188-190] (for example, scheme 15).

$$CCl_2{=}CClCHCl_2 \xrightarrow{SbF_5} CCl_2{=}CClCHF_2 \qquad (15)$$

The process of halogen exchange is usually accompanied by rearrangements[190] and disproportionation[192]. Here there is a tendency to accumulate fluorine atoms at one carbon atom of the chloroalkene.

At high temperatures (100–200°C) complexes of polychloroalkenes with aprotic acids undergo deeper changes; in addition to the halogen exchange dehalogenation and heterolytic breaking of the carbon–carbon bond take place[40,193]. Thus on heating a mixture of hexachloropropene with $AlCl_3$ to 160°C, CCl_4, hexachlorobutadiene, tetrachloroethylene and conversion products of tetrachloroethylene (dichloroacetylene, hexachloroethane, and a polymeric product with conjugated double bonds) are formed[193] (scheme 16).

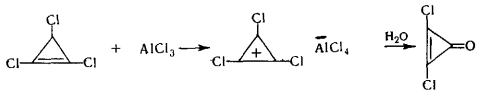
$$CCl_2{=}CClCCl_3\cdot AlCl_3 \rightleftarrows [CCl_2{=}CClCCl_3][\overline{A}lCl_4] \rightleftarrows [CCl_2{=}\overset{+}{C}Cl]\,[\overline{A}lCl_3CCl_3]$$
$$[\overline{A}lCl_3CCl_3] \rightarrow [:CCl_2] + AlCl_4^- \rightarrow CCl_2{=}CCl_2 + AlCl_4^-$$
$$CCl_4 + AlCl_3 \qquad (16)$$
$$\uparrow$$
$$[CCl_2{=}CCl]^+ + [AlCl_4] \xrightarrow{CCl_2=CClCCl_3} CCl_2{=}CClCCl{=}CCl_2 + [\overset{+}{C}Cl_3][\overline{A}lCl_4]$$

In addition to the breaking of the carbon–carbon bond, autocondensation of polychloroalkenes takes place with release of hydrogen chloride and chlorine[187,194] and the production of dimeric compounds. Perchloroalkenes which contain five or more carbon atoms in a chain are readily cyclised under the action of $AlCl_3$ into five- and six-membered rings[4,30], for example, by scheme (17). Here the cyclisation of the perchloroalkenes sometimes takes place with isomerisation of the carbon skeleton[194] and breaking of the carbon–carbon bond.

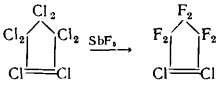
$$CCl_2{=}CClCCl{=}CClCCl_3 \xrightarrow{-Cl_2} \text{(1,2,3,4-tetrachlorocyclopentadiene)} \qquad (17)$$

Thus, heating decachloromethylpentadiene in the presence of $AlCl_3$ leads to the production of CCl_4 and hexachlorocyclopentadiene[195].

The conversions of perchlorinated cycloalkenes, which form extremely stable complexes with aprotic acids, are interesting. The complex of tetrachlorocyclopropene with $AlCl_3$ has the properties of an organic salt, since the trichlorocyclopropylium cation which is formed is very stable[196-201]. On treatment with water, this salt is hydrolysed with release of dichloropropenone according to scheme (18).


(18)

Heating the complexes of perchlorinated cycloalkenes with aprotic acids leads to vigorous exchange of halogens between the cycloalkene and catalyst[199-200] (scheme 19). The allyl chlorine atoms are exchanged first[189]:


(19)

Heating such complexes sometimes leads to the isomerisation of a cycloalkene[203] and to the formation of dimeric products[202]. Dimerisation proceeds with opening of the double bonds[195].

IV. CHLOROALKANES

1. CHLOROETHANES

Chloroethanes are comparatively unstable compounds. Some of them decompose with release of HCl even during storage and distillation. The hydrogen chloride of nonsymmetric chloroethanes is lost most easily[204-206]. To increase the thermal stability of chloroethanes stabilisers are added to them[204-207], for example, aliphatic hydroxyacids[207] and epoxy-compounds[205].

Aprotic acids accelerate the dehydrochlorination of chloroethanes, which, like halogen exchange[212-214], is effected through the intermediate formation of complexes of the $CH_3CH_2Cl.Al_2Cl_6$ type[208-211]. Loss of HCl takes place at temperatures considerably lower than the boiling points of the chloroethanes[215,216]. For chloroethanes with a $CHCl_2$ group the thermal stability in the presence of aluminium chloride increases with the degree of chlorination of the neighbouring methyl group, that is,

$$CH_3CHCl_2 < CH_2ClCHCl_2 < CHCl_2CHCl_2,$$

but drops again on going to pentachloroethane[216]. The rate of dehydrochlorination of chloroethanes with a CH_3 group under the action of the same reagent increases with the content of chlorine atoms in the neighbouring methyl group[216]:

$$CH_3CH_2Cl < CH_3CHCl_2 < CH_3CCl_3 .$$

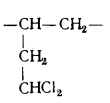
The structure of the initial chloroethanes shows the effect not only on the rate of dehydrochlorination in the presence of aprotic acids but also on the composition of the conversion products of the chloroethanes.

In the presence of $AlCl_3$ at 35–40°C ethyl chloride undergoes a mainly intermolecular dehydrochlorination with the formation of polymeric products with a molecular weight of up to 700 and containing ethylidene units $-\overset{}{\underset{CH_3}{CH}}-$ and carbonyl groups in a ratio of between 10:1 and 30:1.[20] The appearance of carbonyl groups in the polymer is explained[217] by its oxidation at the double bonds. In the reaction of ethyl chloride with $AlCl_3$, in addition to the polymer a little ethylene is also formed, owing to intramolecular $\alpha\beta$-*cis*-elimination of hydrogen chloride from the ethyl chloride. The predominance of intermolecular dehydrochlorination over intramolecular is because there is a high probability of collision of the $CH_3CH_2Cl.AlCl_3$ complexes with one another in the liquid phase. Because the hydrogen in the CH_2Cl group of ethyl chloride is more labile than that in the $-CH_3$ group, intermolecular dehydrochlorination proceeds mainly with involvement of the chloromethyl group. In the dehydrochlorination of ethyl

chloride on metal chlorides ($NiCl_2$, $FeCl_3$, $AlCl_3$) in the vapour phase (300°C) the probability of collision of two molecules of ethyl chloride on the surface of the catalyst is low. Therefore under these conditions there is mainly intramolecular loss of hydrogen chloride with the formation of ethylene[4] and a polymeric product is only produced in small quantities.

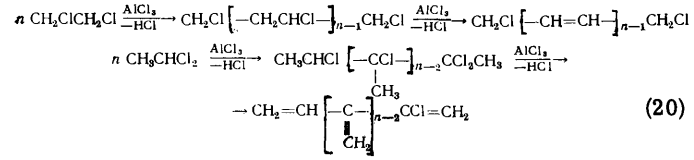
Dichloroethanes. At room temperature and in the presence of small quantities of aluminium chloride there is slight isomerisation of 1,2-dichloroethane into 1,1-dichloroethane[218,219]. This compound is considerably more reactive than its symmetric isomer. Under the action of $AlCl_3$ 1,1-dichloroethane undergoes intramolecular loss of hydrogen chloride with the formation of small quantities of vinyl chloride even at 0°C.[215,219] Furthermore, at 30°C it partly rearranges into the symmetric isomer[219]. At 50–60°C both isomers of dichloroethane undergo intermolecular dehydrochlorination with the quantitative formation of polymeric products with conjugated double bonds[220,221]. The polymeric products of composition $(C_2H_2)_n$ contain predominantly vinylene –CH=CH– (I) and vinylidene $\diagdown C{=}CH_2$ (II) units[221]; they are not polyphenylethylenes, as was suggested earlier[222].

Polymeric products with I and II links cannot be obtained in the dehydrochlorination of poly(vinyl chloride), which is in turn formed by polymerisation of vinyl chloride as already proposed[353]. The present authors heated a mixture of vinyl chloride and $AlCl_3$ under conditions for the polycondensation of dichloroethanes and obtained the same products as were described above (cf. scheme 10). The polymer thus obtained contained mainly the link



and did not contain I units.

Since the reactivities of both the CH_2Cl groups in 1,2-dichloroethane are the same, and in 1,1-dichloroethane the more reactive group is $CHCl_2$,[221] the vinylidene units are formed from 1,1-dichloroethane (scheme 20):



(20)

Mouneyrat[223] obtained tetrabromoethane by heating 1,2-dibromoethane in the presence of bromine and aluminium bromide. From this he concluded that dihalogenoethanes undergo intramolecular dehydrohalogenation on Friedel–Crafts catalysts to acetylene, which then adds bromine and is converted into tetrabromoethane. Evidently, Mouneyrat was wrong, since under the conditions of his experiments the usual bromination, catalysed by aprotic acid[1], should take place. We heated 1,2-dibromoethane in the presence of aluminium bromide or chloride and obtained a polymeric product which is analogous in composition and properties to the polymer obtained from 1,2-dichloroethane.

It is noteworthy that the polymers based on dichloroethanes are, like other poly-conjugated systems[224], thermostabilisers of chlorine-containing compounds[216].

The vapour-phase intramolecular dehydrochlorination of the two dichloroethanes is of interest as an industrial method of obtaining vinyl chloride[225]. The reaction is effected at 300–400°C on acid catalysts (chlorides of zinc, magnesium, iron, aluminosilicate, etc.)[225–228]. Here small quantities of resinous substances are formed as well as vinyl chloride. Furthermore, under these conditions there is also isomerisation of the symmetric isomer of dichloroethane into the non-symmetric[218]. The almost selective dehydrochlorination of dichloroethanes in the vapour phase to vinyl chloride is because here there is little probability of collision of even two molecules of dichloroethane on the catalyst surface. The use of inert gases as diluents has been proposed[229] to even further reduce the probability of such collisions and decrease the formation of resinous substances[229].

1,1,2-Trichloroethane undergoes intramolecular and intermolecular dehydrochlorination in the liquid phase in the presence of $AlCl_3$.[152] Intramolecular elimination of hydrogen chloride to give 1,2-dichloroethylene (mainly the *trans*-isomer)[215] is effected through the intermediate formation of the carbonium ion $CH_2Cl–\overset{+}{C}HCl$. The 1,2-dichloroethylene which is formed reacts further by a cationic mechanism according to scheme (11). The chief reaction which takes place in the reaction of 1,1,2-trichloroethane with $AlCl_3$ is polycondensation with the formation of a polymeric product with conjugated double bonds, including the units –CH=CCl– and $-C(=CHCl)-$ in the ratio 1:1.[152]

In the vapour phase on acid catalysts 1,1,2-trichloroethane undergoes $\alpha\beta$-elimination of hydrogen chloride with predominant formation of *cis*-1,2-dichloroethylene[228,230,231]. Vinylidene dichloride is obtained in addition to 1,2-dichloroethylene[228,230].

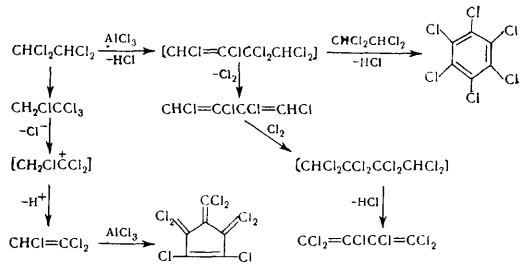
1,1,1-Trichloroethane can be quantitatively converted into vinylidene chloride in the liquid phase under the action of $FeCl_3$.[184,231] In the presence of $AlCl_3$, 1,1,1-trichloroethane also loses hydrogen chloride intramolecularly[150]. However, the vinylidene chloride thus formed is converted further into 1,1,3,3-tetrachlorobutene and 1,1,3,3,5,5-hexachlorocyclohexane under the influence of $AlCl_3$ (cf. scheme 13). The preferential intramolecular dehydrochlorination of 1,1,1-trichloroethane is explained by the fact that this compound, unlike 1,1,2-trichloroethane, gives the relatively stable carbonium ion $CH_3\overset{+}{C}Cl_2$ on reaction with $AlCl_3$. The ionic mechanism of dehydrochlorination of 1,1,1-trichloroethane on acid catalysts[228] is also retained on carrying out the reaction in the vapour phase.

Non-symmetric tetrachloroethane behaves similarly to 1,1,1-trichloroethane in the presence of aprotic acids; in the liquid phase it is smoothly dehydrochlorinated to trichloroethylene[184,215,219,231,232]. Here in addition to trichloroethylene the products are 1,2,3,4,4-pentachlorobutadiene, perchlorofulvene, and 1,2,3,3,5,5-hexachloro-4-(dichloromethylene)cyclopentene[219], which are conversion products of trichloroethylene (see scheme 14).

Non-symmetric tetrachloroethane is smoothly converted into trichloroethylene in the vapour phase on metal chlorides[233,234].

When 1,1,2,2-tetrachloroethane is heated with $AlCl_3$ in the liquid phase, intermolecular dehydrochlorination occurs with the formation of dimeric compounds—1,2,3,4-tetrachlorobutadiene and hexachlorobutadiene—the trimer hexachlorobenzene, and the polymer of composition $(C_6HCl_4)_n$ (scheme 22)[235]. Here the intermolecular elimination of HCl from tetrachloroethane is accompanied by

dechlorination and chlorination, owing to the presence of tetrachlorobutadiene and hexachlorobutadiene among the reaction products. A polymeric product is also the result not only of dehydrochlorination but also the loss of chlorine, and contains five- and six-membered rings.

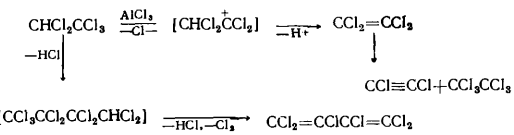


(22)

When 1,1,2,2-tetrachloroethane is heated with $AlCl_3$ in addition to polycondensation it undergoes isomerisation into the non-symmetric isomer[235,236], which under the conditions of the reaction loses HCl intramolecularly with the formation of trichloroethylene.

Dehydrochlorination of symmetric tetrachloroethane on acid catalysts in the vapour phase leads to a mixture of products in which trichloroethylene predominates[228]. In addition to trichloroethylene, tetrachloroethylene, pentachloroethane, and hexachloroethane are also observed[237]. Probably, dehydrochlorination of tetrachloroethane in the vapour phase takes place by a radical mechanism.

Pentachloroethane, like other chloroethanes with the CCl_3 group, forms the stable carbonium ion $CHCl_2-\overset{+}{C}Cl_2$ in the presence of aprotic acids, and this ion is further converted into tetrachloroethylene[215,219,238,239]. In the presence of large quantities of $AlCl_3$ (pentachloroethane : $AlCl_3$ ratio 5 : 1) in the liquid phase (120–150°C) dichloroacetylene, hexachloroethane, and hexachlorobutadiene are formed in addition to tetrachloroethylene[219]. The conversion of pentachloroethane under these conditions take place by scheme (23).



(23)

Tetrachloroethylene is the only product of the pyrolysis of pentachloroethane in the vapour phase (200–350°C) in the presence of aprotic acids[30,240].

Hexachloroethane is very stable on heating, as [might be expected of] a symmetrically constructed compound[30]. In the presence of aprotic acids at 200–250°C (in an ampoule) it does not undergo any changes in the liquid phase[19]. In the vapour phase at 300–400°C on Lewis acids, hexachloroethane is destroyed by a radical mechanism with the formation of tetrachloroethylene and chlorine[25–27].

2. SUBSTITUTED CHLOROETHANES

Replacement of the chlorine atoms in chloroethanes by more electronegative groups (*p*-chlorophenyl[241], fluorine[242]) retards the dehydrochlorination of chloroethanes. In addition there is an increase in the tendency of chlorofluoroethanes to undergo rearrangements[42,242–245]. Isomerisation of chlorofluoroethanes in the presence of aprotic acids proceeds in such a manner that the fluorine atoms are grouped on one carbon atom with the formation of the CF_3 group[245]. In addition to isomerisation there is an exchange of halogen atoms between catalyst and chlorofluoroethane. The introduction into chloroethane of the trichlorosilyl group considerably accelerates the dehydrochlorination of chloroethanes under the action of $AlCl_3$.[246–249] The main direction of this reaction is intramolecular dehydrochlorination with the formation of silicon-containing alkenes[247]. For 2-chloroethylsilane, in addition to dehydrochlorination under the action of $AlCl_3$ there is appreciable elimination of $SiCl_4$.[250–252] This process can proceed with quantitative formation of $SiCl_4$[250] (scheme 24).

$$CH_2ClCH_2SiCl_3 \xrightarrow{AlCl_3} CH_2{=}CH_2 + SiCl_4$$
$$CH_3CHClSiCl_3 \xrightarrow{AlCl_3} CH_2{=}CHSiCl_3 + HCl\,. \qquad (24)$$

3. HIGHER CHLOROALKANES AND CHLOROCYCLOALKANES

Higher chloroalkanes, like chloroethanes, form complexes with halides of coordination-unsaturated metals[253–255] in which there is exchange of halogens between the chloroalkane and the salt[253,256–262]. It has been noted[253–255] that halogen exchange is greatly accelerated when hydrogen chloride is introduced into the reaction mixture.

Aprotic acids bring about various rearrangements of chloroalkanes[157,263,264]. The most frequently encountered rearrangement is the transfer of chlorine atoms from one carbon atom to another[254,255,265–270]. Here the chlorine is usually transferred to the carbon with the greatest number of substituents, that is, from a primary to a secondary to a tertiary. Thus, under the action of $AlCl_3$ propyl chloride is completely isomerised into isopropyl chloride[265]. It is assumed that such isomerisation proceeds by a pseudo-ionic mechanism in an intermediate five-membered complex[255].

Under the influence of aprotic acids, when heated in the liquid phase chloroalkanes readily lose hydrogen chloride[6,266,267,271–275]. Here the chloroalkanes with CCl_3 groups and also alkyl chlorides containing chlorine atoms at secondary and tertiary carbon atoms are usually dehydrochlorinated to alkenes[184,276–286]. Under the action of aprotic acids primary alkyl chlorides are either isomerised[254,255,265–274] into secondary and tertiary alkyl chlorides, which then lose hydrogen chloride intramolecularly, or react by intermolecular dehydrochlorination, which leads to the formation of higher-molecular-weight products[6,270–272]. Thus Friedel and Crafts obtained a dimeric compound (chlorodecane) from pentyl chloride[271,272]. On reaction with aprotic acids compounds with the CCl_3 group are ionised with the formation of carbonium ions[287–289], which are converted by different paths. When a proton is present at a neighbouring carbon atom it is removed and an alkene is formed[4,193,280,281,290]. In the absence of such a hydrogen atom the carbocation can react by the breaking of carbon–carbon bonds[193,290–292] (scheme 25):

$$CHCl_2CCl_2CCl_3 + AlCl_3 \rightleftarrows [CHCl_2CCl_2\overset{+}{C}Cl_2][\overline{AlCl_4}] \rightarrow CCl_2{=}CCl_2 + [\overset{+}{C}HCl_2][\overline{AlCl_4}]$$
$$[\overset{+}{C}HCl_2][AlCl_4] \rightarrow CHCl_3 + AlCl_3 \qquad (25)$$

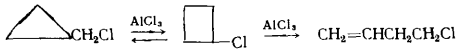
Perchlorinated alkanes with a long carbon chain (not less than C_5) are cyclised under the action of aprotic acids[30,293].

The main reaction of chloroalkanes in the presence of salts of coordination-unsaturated metals in the vapour

phase at 300–600°C is dehydrochlorination. In this the regularities which are observed in the liquid phase are retained. The dehydrochlorination of the long-chain chloroalkanes is accompanied by the isomerisation of the carbon skeleton[294], the transfer of the double bond along the carbon chain[295,296], and the breakage of a carbon–carbon bond, which leads to the formation of a mixture of alkenes. Completely chlorinated hydrocarbons are decomposed in the vapour phase under the action of Lewis acids with breakage of a C–C bond to give tetrachloroethylene and CCl_4.[297,298]

Chlorocycloalkanes. The conversions of 1,2,3,4,5,6-hexachlorocyclohexane and other chlorinated cyclohexanes have been studied in greatest detail. At moderate temperatures (20–120°C) the reaction of the chlorocyclohexanes with $AlCl_3$ is brought about by exchange of chlorine atoms between catalyst and chlorocyclohexane[299], by the migration of chlorine atoms in the cyclohexane ring[300] and by spatial isomerisation[299–301]. For example, under the action of $AlCl_3$ at 20°C *trans*-1,2-dichlorocyclohexane is partly converted into *cis*-1,2-dichlorocyclohexane and is isomerised to *cis*- and *trans*-1,4-dichlorocyclohexane. On heating γ-1,2,3,4,5,6-hexachlorocyclohexane to 112°C with $AlCl_3$ labelled with the isotope ^{36}Cl there is a vigorous exchange of chlorine isotopes between the catalyst and the hexachlorocyclohexane[299]. Furthermore, isomerisation of the γ-isomer into the α-isomer takes place[299–301]. It is noteworthy that when heated with aprotic acids all the isomers of hexachlorocyclohexane are converted into the α-isomer, the configuration of which is most favourable energetically[301]. At high temperatures (250–400°C) chlorinated cyclohexanes lose hydrogen chloride readily under the influence of aprotic acids[301–305]. Thus hexachlorocyclohexane is dehydrochlorinated in the presence of $FeCl_3$ with the formation of 1,2,4-trichlorobenzene and of its isomerisation product 1,2,3-trichlorobenzene[301]. Here the α-isomer is dehydrochlorinated with greater difficulty than the other hexachlorocyclohexane isomers.

Cyclobutyl chloride and cyclopropylmethyl chloride undergo initial conversions under the action of $AlCl_3$.[306] Cyclopropylmethyl chloride readily rearranges at −40°C into cyclobutyl chloride and 1-chlorobut-3-ene (scheme 26):

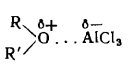


(26)

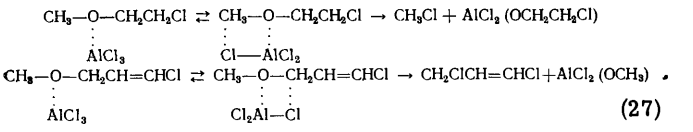
The rearrangement of cyclobutyl chloride into cyclopropylmethyl chloride and 1-chlorobut-3-ene takes place at a higher temperature (+15°C). Kinetic investigations[306] of these conversions show that the rearrangements have an ionic mechanism.

4. SUBSTITUTED CHLOROALKANES

Chloroalkanes which incorporate other halogens (fluorine or bromine) readily disproportionate in the presence of aprotic acids[266,307]. The introduction of alkoxy-groups into chloroalkanes accelerates their dehydrochlorination[308]. The reaction centre of alkoxychloroalkanes in their reaction with aprotic acids could be the ether group. Complexes of the type



are formed, which decompose when heated, with the formation of aluminium alkoxides and chloroalkanes[309]. The ether decomposes in such a way that the radical split off in the form of a halogenoalkane is that which has most tendency to acquire part of the positive charge from the oxygen atom. For example, when 2-chloroethyl methyl ether reacts with $AlCl_3$ it decomposes with liberation of methyl chloride[309], whereas 1,3-dichloro-prop-2-ene is formed from 3-chloroprop-2-enyl methyl ether[310] (scheme 27):



(27)

When the alkoxy-group in the chloroalkanes is in proximity to reactive CCl_3 or CHCl groups, which exhibit labile chlorine atoms, then the conversion of such compounds in the presence of aprotic acids leads to the formation of epoxy-compounds which are subsequently rearranged into ketones and acyl chlorides[311].

When γ- and δ-chlorine-containing ethers are heated with $FeCl_3$ or $SbCl_5$ they are cyclised with the formation of oxacycloalkanes[312–315]. For example, tetrahydrofuran and the metal chloride are formed in high yield from 4-chlorobutyl methyl ether in the presence of $FeCl_3$.[315]

Chloroalkanes which include phenyl groups readily undergo autocondensation under the conditions of the Friedel–Crafts reaction with release of hydrogen chloride and formation of cyclic and linear compounds[316–318]. Thus on heating a mixture of 1-chloro-1-phenylethane and $AlCl_3$ two molecules of the former are condensed and 9,10-dihydro-9,10-dimethylanthracene is obtained[312]. When in a chloroalkane there are 3–5 carbon atoms between the chlorine atom and the phenyl group, such compounds undergo cycloalkylation[319].

5. CHLORO-CONTAINING POLYMERS

The reactions of salts of coordination-unsaturated metals with polymers which are widely used in industry have been most studied. They include homopolymers and copolymers of vinyl chloride and vinylidene chloride and also chlorinated poly(vinyl chloride), which consist of the units $-CH_2-CHCl-$, $-CHCl-CHCl-$, and $-CH_2-CCl_2-$. When these polymers are heated they decompose with liberation of hydrogen chloride[320–323]. Many investigations devoted to the dehydrochlorination of poly(vinyl chloride) (PVC) showed that loss of hydrogen chloride takes place by ionic[322,324], pseudo-ionic[322,325], and radical[321–323] mechanisms. In the presence of salts of coordination-unsaturated metals the dehydrochlorination of PVC is accelerated[320–322,326–331] and proceeds by a pseudoionic mechanism[325,327,328]. Here the rate of dehydrochlorination is even greater when the salts of coordination-unsaturated metals and the hydrogen chloride liberated form rather stable complexes of the type MX.HCl,[322,332–334] which catalyse the decomposition of the polymer, owing to their acidic nature. The dehydrochlorination of PVC under the action of aprotic acids is effected both intramolecularly (which leads to a system of conjugated double bonds[335–338]) and also intermolecularly, as a result of which a structured, insoluble polymer is formed[339]. Furthermore, destruction of the PVC with breaking of the carbon–carbon bond is observed[340]. Organic solvents, such as dimethylformamide and aromatic amines, which form stable complexes with aprotic acids, decrease the catalytic action of these salts, as a result of which the rate of dehydrochlorination of PVC decreases considerably[341–343].

To suppress the dehydrochlorination of chlorine-containing polymers in their manufacture into various articles, stabilisers are usually employed. Salts of coordination-unsaturated metals are used as stabilisers for PVC [320,321,344,345]. They include aluminium, zinc, cadmium, and lead salts of stearic, lauric, caprylic, and other organic acids, and also the dicarboxylates of dialkoxides [320,321]. In addition, basic lead salts of organic and inorganic acids find wide application. The stabilising action of these salts is based on both the bonding of the hydrogen chloride released in the destruction of the polymers and on their reaction with the labile chlorine atoms of the polymer [346-349]. In the latter instance there is exchange of the chlorine atoms in the tertiary alkyl chloride and allyl chloride groupings which are present in commercial PVC [350], by the acyl residues of the salts [333,334,346-349,351] with the formation of ester groups (scheme 28):

$$-\overset{|}{\underset{Cl}{C}}- + Pb(OCOR)_2 \rightarrow -\overset{|}{\underset{OCOR}{C}}- + PbCl(OCOR) . \qquad (28)$$

Since the sub-units which contain the ester groups are more stable thermally than the sub-units with labile chlorine atoms [352] the resistance of the polymer to dehydrochlorination is enhanced as a result of this reaction [333,334,351]. The stabilising action of certain salts of coordination-unsaturated metals is also based on the fact that they form complexes with reactive groups of the polymer (conjugated double bonds, oxygen-containing groups) which give it a colour [332-334]. As a result of complex formation by chromophoric groups with a stabiliser the colour of the polymer is reduced.

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Hence the principal reaction of hydrogen-containing organochlorine compounds under the action of aprotic acids is dehydrochlorination, which is intramolecular or intermolecular, depending on the structure of the initial organochlorine compound. Intramolecular elimination of hydrogen chloride takes place through the intermediate formation of relatively stable carbonium ions and leads to the formation of alkenes. Intermolecular dehydrochlorination is effected by simultaneous electron transfer to the transition complex, as a result of which a higher-molecular-weight compound is obtained. In the presence of $AlCl_3$ certain chloroethanes (dichloroethanes, 1,1,2-trichloroethane, 1,1,2,2-tetrachloroethane) can give high yields of polymers with conjugated double bonds which exhibit semiconducting properties. Dehydrochlorination is usually accompanied by parallel processes, such as cationic polymerisation of chloroalkenes, isomerisation, rearrangements, disproportionation, halogen exchange between chlorine-containing compounds and the catalyst, cyclisation, complex formation, breaking of –C–C–, –C–O– and other bonds, dehalogenation, which mainly proceed by ionic or pseudoionic mechanisms. The conditions for the reaction of organochlorine aliphatic compounds with the salts of coordination-unsaturated metals have a marked effect on the direction of these reactions. As a result suitable choice of the reaction conditions enables certain of the above processes to occur preferentially and desirable products to be obtained in high yields.

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Addition Reactions with Intramolecular Cyclisation

V.I.Staninets and E.A.Shilov (deceased)

Heterolytic addition reactions in which the effect of the electrophilic agent on a double or triple bond leads to intramolecular cyclisation via an electron-donating group ("the AC reaction") are discussed. These reactions almost always give rise to five- and six-membered rings. Weak electrophilic agents form only cyclic adducts under the conditions of AC reactions, while strong electrophilic agents form, together with cyclic compounds, simple and mixed acyclic addition products. The formation of cyclic adducts is also promoted by the rigid structure of the unsaturated molecule and the nucleophilic properties of the electron-donating group.
The AC reactions obey the kinetic equations for second-order processes. They are distinguished from the analogous trimolecular acceptor-donor addition reactions by the synchronous occurrence of the electrophilic and nucleophilic stages in the elementary step, which is related to the steric conditions of ring formation.
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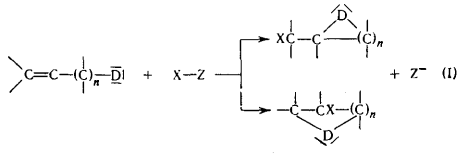
I. INTRODUCTION. THE CONCEPT OF ADDITION REACTIONS WITH CYCLISATION

Reactions where the addition of an electrophilic agent X–Z to an unsaturated molecule containing an electron-donating group D is accompanied by the formation of a heterocycle via the mechanism (two possible modes of these reactions are shown)



(I)

are of particular interest. Unsaturated molecules in which the double bond is incorporated into a cyclic system and also compounds with a triple bond or with heteroatoms in the carbon chain react via mechanism (I). Addition reactions with cyclisation of this type will be referred to as AC reactions.

On the one hand AC reactions have found practical application in the synthesis of a wide variety of heterocyclic compounds. On the other hand, they are of considerable theoretical interest because their study can yield certain new information about heterolytic addition reactions.

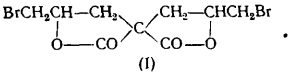
In the literature there are no reviews of reactions of this type—only individual cases and special relations in such reactions are noted in reviews on other topics, in particular those where the problem of "the effect of neighbouring groups" is discussed[1-5].

This review deals with the effect of the structure of the reactants on the nature of AC reactions, the relevant kinetic data are presented, and a general theoretical interpretation of these reactions is given.

The formation of lactones and other cyclisation reactions under the influence of acids are not discussed because they have been partly reviewed elsewhere[3,4] and because the extensive literature data on these reactions merit a discussion in a separate article.

II. STRUCTURAL FACTORS IN ADDITION REACTIONS WITH CYCLISATION

The intramolecular formation of cyclic species in addition reactions was first observed by Fittig and Hjelt[6] in the bromination of diallylacetic and diallylmalonic acids. Structural formulae with a five-membered ring were ascribed to the resulting bromolactones, for example structure (I) for the bromination product of diallylmalonic acid:

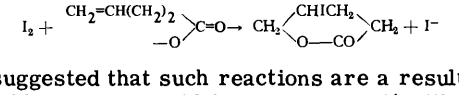


(I)

In order to account for the formation of bromolactones, Fittig and Hjelt assumed the intermediate formation of unstable dibromides, which cyclise with elimination of hydrogen bromide. We may note that similar hypotheses were also put forward subsequently in the discussion of the mechanism of AC reactions.

The intramolecular formation of cyclic species was observed also in the study of the reactions of allylureas and allylthioureas. When these compounds were brominated or iodinated, bromomethyl- or iodomethyl-oxazolidines and thiazolidines were obtained[7,11].

Bougault[12-14] made a detailed and systematic study of the formation of iodine-substituted lactones in the iodination of unsaturated carboxylic acids in aqueous potassium iodide and sodium bicarbonate solutions, i.e. under conditions where the acids are present in the form of anions, for example:



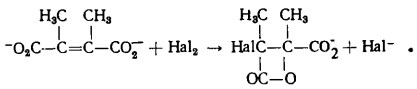
He also suggested that such reactions are a result of the addition of hypoiodous acid *in statu nascendi* with subsequent lactonisation of the resulting iodoxy-acid. He showed that only those unsaturated compounds whose structure allows the formation of a five- or six-membered

ring are capable of iodolactonisation reactions. Subsequently numerous examples showed that this rule is extremely general for AC reactions.

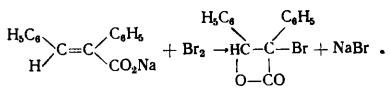
If the structure of the unsaturated molecule does not allow the formation of a five- or six-membered ring, then iodination under the conditions of the Bougault reaction does not occur at all or leads to unstable non-cyclic adducts—di-iodides and iodohydrins.

In particular, acrylate and crotonate anions and their substituted derivatives, the structure of which allows the formation of only four-membered rings, do not react with iodine. Octenic acids, and probably other unsaturated acids in which the electron-donating group is separated from the double bond by more than six atoms, do not form iodolactones[13,15].

However, it is noteworthy that the bromination or chlorination of unsaturated dimethylmaleate and dimethylfumarate anions leads to the rare case of the formation of a four-membered lactone[16]:

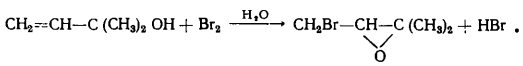


A similar four-membered lactone was obtained recently[7] by the bromination of the sodium and silver salts of *cis*- and *trans*-stilbene-2-carboxylic acids in carbon tetrachloride:



The reaction is accompanied by the formation of polymers and side products. The configuration of the resulting lactone was not indicated.

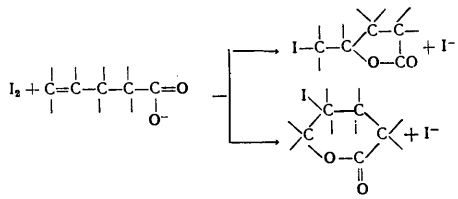
The formation of a three-membered ring was observed in the bromination of dimethylvinylmethanol[18]:



The exclusive formation of five- and six-membered rings in AC reactions has been used for the iodometric determination of $\beta\gamma$- and $\gamma\delta$-unsaturated acids in mixtures with acids having other structures[19]. The composition of mixtures of compounds containing *endo*- and *exo*-bridges (in the form of CH_2 and CH_2CH_2 groups) has been determined similarly[20-22]. Under certain conditions of analysis, only the *endo*-compounds are iodinated.

Bougault established that the derivatives of but-3-enoic acid (4-ethyl, 4-phenyl, 4-benzyl, 4-anisyl, 2,2-dimethyl, 2,4-diphenyl-, 2,2,4-trimethyl-, and other derivatives) form only five-membered iodolactones, in accordance with their structures[13]. Subsequently analogous iodolactones were obtained from 4-methyl-, 4-vinyl-, and 4-ethyl-pent-3-enoic acids[15,23,24]. However, unsubstituted but-3-enoic (vinylacetic) acid reacts with difficulty and, as shown recently[24], forms iodine-free furanones (4-hydroxy-2-oxotetrahydrofuran, its vinylacetic ester, and 2-oxo-3,4-dihydrofuran). These compounds are probably formed as a result of the hydrolysis and elimination of hydrogen iodide from the intermediate iodo-adducts.

Compounds with the structure of pent-4-enoic (allylacetic) acid can form both five- and six-membered rings:



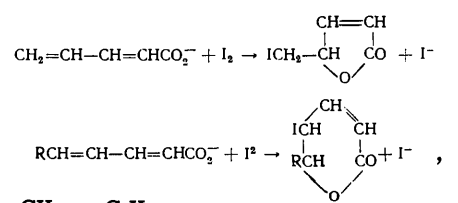
Few reliable data have been published on the mode of cyclisation in those reactions where there is a possibility of the formation of both five- and six-membered rings. In many cases the structures of the resulting cyclic adducts were not established or are only tentatively indicated. This is because the chemical methods for distinguishing five- and six-membered rings are fairly laborious. At the present time spectroscopic methods (infrared and NMR spectroscopy) are being used with great success[25-27].

It has been shown[23] that on iodination unsubstituted pent-4-enoic acid forms only a five-membered iodolactone†. Five-membered iodolactones are also formed from 1- and 3-cyclohexenylacetic acids[23]. However, hex-4-enoic acid gives rise to a six-membered iodolactone[24]. Iodination of *cis*-cinnamylacetic acid results in the formation of a five-membered lactone, while its *trans*-isomer gives a mixture of compounds with five- and six-membered rings[28].

The addition of electrophilic agents in AC reactions involving the competing formation of five- or six-membered rings in general takes place in accordance with the Markovnikov rule. However, the mode of reaction depends not only on the electronic nature of the substituents at the C=C bond but also on the steric effects of these substituent on the stabilisation of the cyclic transition state and on the nucleophilic properties of the electron-donating end of the unsaturated molecule. Therefore an exact prediction of the structure of the AC reaction product is not always possible.

Especially little is known about the effect of electron-accepting groups at the C=C bond on the mode of cyclisation. This is because electron-accepting substituents greatly hinder or even prevent the addition of weak electrophilic agents via the AC reaction mechanism.

If the unsaturated chain of the compound iodinated contains two conjugated double bonds, the rule of the formation of a five- or six-membered ring holds, but the iodocyclisation reaction is retarded[24]. The vinylacrylate anion gives the iodolactone with the dihydrofuran structure and hexa-2,4-dienate (sorbate) and 5-phenylpenta-2,4-dienate anions form six-membered rings on iodination[24]:



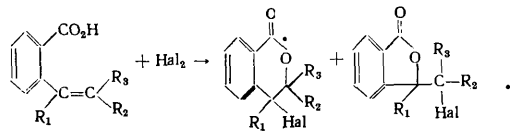
where R = CH_3 or C_6H_5.

Evidently in the reaction with iodine the terminal carbon atom is more active in the CH_2=CH group, while in the RCH=CH group the electrophilic agent acts upon the

† Bougault suggested that the iodolactone from allylacetic acid has a pyran structure[13]. This error was amended by van Tamelen and Shamma[23].

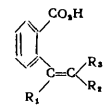
neighbouring carbon atom and ring closure occurs at the atom linked to the R group. Thus the rule established for allyl derivatives holds for compounds with conjugated double bonds.

If the hydrogen atoms in *o*-vinylbenzoic acid are substituted by alkyl groups, iodination results in the formation of both five- and six-membered iodolactones or their mixture:



Berti and coworkers[29-35] investigated the chlorination of 2-vinylbenzoic acids in carbon tetrachloride and in water and their bromination in chloroform and acetic acid. Their results are presented in Table 1, which shows that the accumulation of substituents at the terminal atom of the vinyl group leads to the formation of a six-membered ring, while substitution at the neighbouring atom promotes the formation of the furan ring.

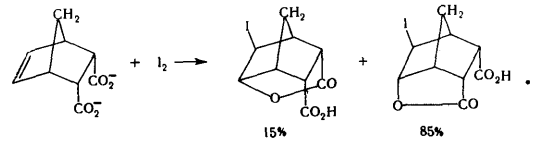
Table 1. Mode of halogenocyclisation of 2-vinylbenzoic acids[35]



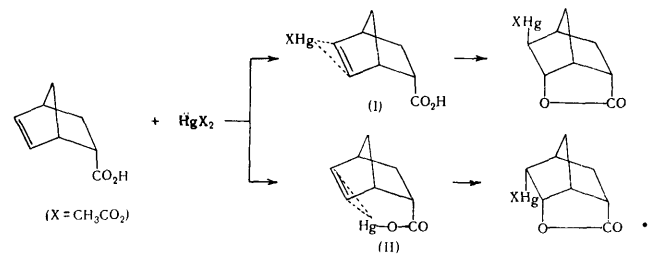
R_1	R_2	R_3	No. of units in ring after reaction with Cl_2	No. of units in ring after reaction with Br_2	R_1	R_2	R_3	No. of units in ring after reaction with Cl_2	No. of units in ring after reaction with Br_2
CH_3	H	H	5	5	H	CH_3	CH_3	6	—
C_6H_5	CH_3	H	5	5	H	C_6H_5	H	6	6
iso-C_3H_7	CH_3	CH_3	6	6	CH_3	C_6H_5	H	5+6	—

The effect of geometrical isomerism on the formation of five- and six-membered iodolactones was investigated in the iodocyclisation of cinnamylacetic acid and its $\beta\beta'$-disubstituted derivative[28]. *cis*-Cinnamyl acetic acid forms only a five-membered adduct, while the *trans*-isomer gives a mixture of five- and six-membered iodolactones; *cis*-$\beta\beta'$-dimethylcinnamylacetic acids gives rise to a mixture of both products and the *trans*-isomer only the six-membered iodolactone.

AC-reactions have the same fundamental mechanism (I) also in those cases where the double bond is in a ring, provided that the formation of a five- or six-membered ring is possible. Examples of such reactions are known for tetrahydrobenzoic[19,21-23,36] and tetrahydrophthalic acids; their bridged derivatives[37-51], and dihydronaphthoic[52] and cyclohexenylacetic acids[13,23,53]. Iodination and mercuration of these compounds in an aqueous medium usually results in the formation of five-membered rings even in those cases where the structure of the compounds allows the formation of a six-membered ring[24]. A mixture of five- and six-membered iodolactones is obtained in the iodination of *cis*-3,6-*endo*-methylene-Δ^4-tetrahydrophthalate salts[49]:

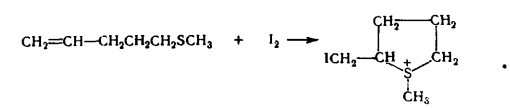


The formation of a mixture of stereoisomeric five-membered lactones in the mercuration of 2,5-*endo*-methylene-Δ^3-tetrahydrobenzoic acid with mercury acetate was noted[54]. The authors explained the formation of the five-membered *cis*-mercurilactone by the intermediate formation of the complex (II):



In contrast to the *endo*-series, unsaturated acids of the *exo*-series do not form lactones on iodination or mercuration, probably because the carboxylate ion is sterically hindered by the methylene group[21,22,43,49,54].

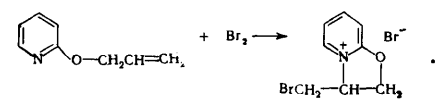
The general rules for AC reactions operate also in those cases where the ring closure does not take place via the carboxylate group but via another electron-donating group. $\gamma\delta$-Unsaturated alcohols, sulphides, and amines give rise on iodination or bromination to five-membered tetrahydrofuran, tetrahydrothiophen, and tetrahydropyrrole derivatives[15,55,56], for example:



o-Allylphenol and 2-allyl-4,6-dichlorophenol form iodomethylbenzotetrahydrofurans. α-(ω-Butenyl)pyridine is converted into 2-iodomethyl-1,5-pyridopyrrolidinium iodide[56].

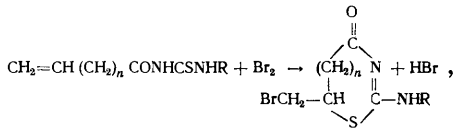
When the chain of the unsaturated molecule contains a heteroatom or a group Δ = O, S, or NH, the iodocyclisation reactions become relatively hindered and in many cases acyclic addition or substitution takes place[57-60]. The compounds $CH_2{=}CHCH_2{-}\Delta{-}CH_2CO_2^-$ and $CH_2{=}CHCH_2{-}\Delta{-}CH_2CH_2N(CH_3)_2$ give rise only to six-membered adducts[57]. It is interesting that a seven-membered ring is not formed on iodination even in those cases where the structure of the initial compound promotes its formation. Thus iodination of the allyloxy-β-propionate ion does not give a cyclic adduct, which could have been only seven-membered in this case[57]. Allyloxymethylamines are iodinated with formation of five-membered rings[61].

When α-allyloxy- and α-allyl-aminopyridines are brominated[56], the closure of the five-membered ring takes place at the nitrogen atom:



There exist examples of ring closure in addition reactions at chains containing several heteroatoms. Thioureas

acylated by residues of $\alpha\beta$-, $\beta\gamma$-, and $\gamma\delta$-unsaturated carboxylic acids react with bromine in carbon tetrachloride and chloroform via the mechanism[62,63]

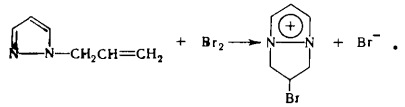


where R=H, alkyl, or aryl and n = 0, 1, or 2.

An interesting case of the formation of a seven-membered ring[63,64] (4-thiazepinone) with n = 2 has been described.

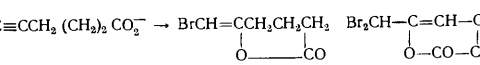
These bromocyclisation reactions are accompanied by the addition of bromine at the double bond, but in the formation of a five-membered thiazoline ring (n = 0) there are no dibromides in the reaction products or their amount is very small, while in the case of larger rings the yield of dibromide is appreciable.

The bromination of 1-allylpyrazole results in a derivative of 3a,6a-diazapentalene[65,66]:

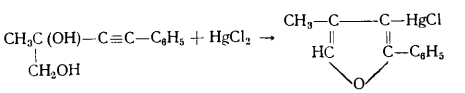


Not many AC reactions for compounds with a triple bond are known. The replacement of a double bond by a triple bond leads to the retardation of the reaction, but in all probability the general rules of AC reactions remain in force. As a result of addition, a compound with an electron-donating group at the double bond is formed in the first stage. This frequently leads to further reactions.

The iodination of propargylacetic and propargylmalonic acids stops at the stage involving the formation of an unsaturated, probably five-membered, lactone[15,67]. In the bromination of hex-5-ynoic acid[68] the reaction proceeds further and yields an unsaturated dibromide:



Primary-tertiary and secondary-tertiary butynediols are converted by mercury(II) chloride into chloromercurifurans[69-72]:



Amines and oxamines containing the propargyl group, $HC\equiv C-CH_2OCH_2NHR$, $HC\equiv C-CH_2OCH_2NR_2$, and $HC\equiv C-CH_2(CH_2)_2NR_2$, also cyclise to five-membered ring compounds on bromination and iodination[61].

III. EFFECT OF THE NATURE OF ELECTRON-DONATING GROUPS AND X–Z ELECTROPHILIC AGENTS IN ADDITION REACTIONS WITH CYCLISATION

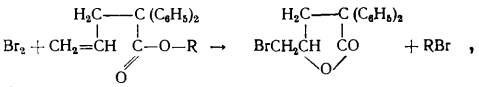
1. Electron-donating Groups

Ring closure in addition reactions takes place with participation of various electron-donating groups: OH, RO^-, NH_2, NHR, NR_2, –SR, CO_2^-, CO_2H, COOR, $\rangle C{=}O$, $CONR_2$, $CSNR_2$, etc. The capacity of these groups for ring closure depends on their nucleophilic properties. Weakly nucleophilic electron-donating groups, for example RSO_3^-, are incapable of ring closure on iodination[15,73]. However, under the influence of powerful electrophilic agents (bromine and chlorine), the same unsaturated sulphonate salts form sultones[74].

Unsaturated amines cyclise only in the form of the free bases with formation of ammonium salts[15,75].

Phenoxides react much more readily than the free phenols[15,76,77], but in the case of unsaturated alkoxides ring closure was not observed, probably owing to the low concentration of the alkoxides in aqueous solutions at low pH.[76,78,79] The free carboxy-group can participate in ring closure, but the conjugate carboxylate anions react much more readily. Therefore it sometimes happens that in aqueous solutions of unsaturated acids the anion and not the undissociated acid itself reacts with the electrophilic agent.

It is remarkable that, under the influence of powerful electrophilic agents, even the ester group can form a lactone with elimination of an alkyl halide[80-83]:



The iodination of the amides of unsaturated carboxylic acids in acidic and neutral aqueous solutions results in the formation of lactims, while in alkaline solutions the products are lactams[15,84-87]. When 2,2-disubstituted allylacetonitriles are brominated in chloroform, lactims are formed together with dibromides[85]. On bromination, allylacetamidomalonic ester yields 6-bromomethyl-4,4-diethoxycarbonyl-2-methyl-5,6-dihydro-1,3-oxazine dibromide[86].

The bromination of allylureas gives 5-bromomethyl-Δ^2-oxazolines together with dibromides[9,88-91]. In contrast, allylthioureas form on bromination and iodination only 5-bromomethyl-Δ^2-thiazolines[7,8,10,11,92-94].

Probably many other electron-donating groups can also participate in AC reactions (for example the epoxy-, N-oxide, oxime, etc. groups, which have not yet been investigated).

Williams et al.[95] recently published a paper in which the results of a study of the bromination and iodination of the alcohols $CH_2{=}CH(CH_2)_nOH$, where n = 1, 2, 3, or 4, are presented. They show a close analogy between the reactions of these alcohols and the halogenation of the acids $CH_2{=}CH(CH_2)_{n-1}CO_2H$. In particular, the maximum rate occurs with n = 3, which corresponds to the formation of a five-membered ring. Bromination results in a mixture of cyclic and non-cyclic addition products (50–60% of cyclic products with n = 3, 5–10% with n = 4, and 0% with n = 1 or 2). Iodination of the alcohols with n = 3 and 4 gives only the cyclic adducts. The quantitative characteristics of the involvement of electron-donating groups in ring closure will be presented in the discussion of the kinetic relations in AC reactions.

2. Electrophilic Agents

Among the known electrophilic agents, iodine, bromine, chlorine, iodine chloride, cyanogen iodide, hypochlorous acid, mercury salts, peracids, 2,4-dinitrosulphenyl chloride, and tellurium and selenium compounds have been investigated in AC reactions. Strong acids can also behave as electrophilic agents in AC reactions but, as already stated, such reactions are not discussed in this review.

Certain electrophilic agents, for example $SnCl_4$, ArN_2^+, etc., have not been tested in AC reactions.

The mode of addition depends on the differences between the electrophilicities of the reactants. Weak electrophilic agents (I_2, $HgCl_2$) often react wholly via the AC reaction mechanism. This applies particularly to those cases where the electrophilic agent (for example I_2 in aqueous KI solutions) is altogether incapable of adding to unsaturated molecules via the usual mechanism. Strong electrophilic agents show a greater tendency to form non-cyclic adducts, particularly in non-aqueous solvents.

According to the literature, in the bromination of many unsaturated acids in non-ionising solvents only the dibromides were isolated even in those cases where bromolactones could have been formed. Incidentally, it is possible that in some cases small amounts of cyclic adducts escaped the notice of investigators.

According to Berti's data, the bromination of *cis*- and *trans*-stilbene-2-carboxylic acids gives a mixture of dibromides and bromolactones. The mixture compositions are different for the two stereoisomers and depend on the nature of the solvent. In particular, the reaction of the *cis*-acid with bromine in carbon tetrachloride results in the almost exclusive formation of the dibromide, while in chloroform the product is mainly the bromolactone.

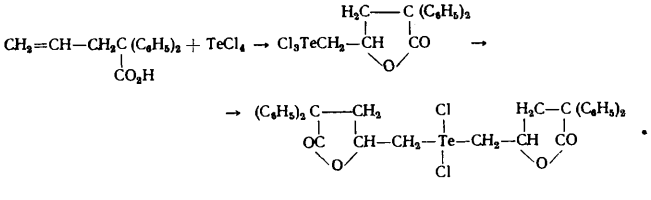
It is interesting that the chlorination of these acids in acetic acid as well as in chloroform and carbon tetrachloride leads to quantitative formation of the chlorolactones.

Data are available on the relative amounts of the cyclic and non-cyclic adducts in the chlorination and bromination products of certain unsaturated compounds in an aqueous medium[96]. Table 2 shows that, when salts of unsaturated acids are brominated and chlorinated, the yield of the halogenolactones is much lower than in iodination, since their iodination takes place with quantitative formation of iodolactones alone. In the reactions with chlorine the amount of lactones formed is much less than in the reactions with bromine (in contrast to Berti's observations in non-aqueous solvents).

Table 2 also shows that compounds with rigidly fixed reaction centres such as the anions of 3,6-*endo*-methylene-Δ^4-cyclohexene-1,2-dicarboxylic acids give higher yields of halogenolactones on chlorination and bromination than the anions of Δ^4-cyclohexene-1,2-dicarboxylic acids, the structure of which permits the inversion of the cyclohexene ring.

Electrophilic agents can participate in AC reactions in different forms. Thus it has been shown that mercury(II) chloride reacts both as $HgCl_2$ and $HgCl^+$, the chloromercury cation being 120 000 times more active than the neutral molecule[97,98]. Moreover, iodine never participates in AC reactions as the iodine cation (more precisely its complex with the substrate molecule), although this form of iodine is the most important active agent in aromatic substitution reactions[99].

Among complex electrophilic agents, 2,4-dinitrobenzenesulphenyl chloride, which readily adds to unsaturated molecules via the usual mechanism but can participate also in AC reactions, is of interest. Tellurium tetrachloride forms 1 : 2 cyclic adducts with $\alpha\alpha'$-diphenylallylacetic acid:



Unsaturated carboxylic acids also cyclise when acted upon by ring-substituted phenylselenium bromides and β-naphthyltellurium iodides[100,101].

In the reaction with peracids as electrophilic agents *cis*- and *trans*-stilbene-2-carboxylic acids are converted into mixtures of epimeric five- and six-membered hydroxylactones[32], for example:

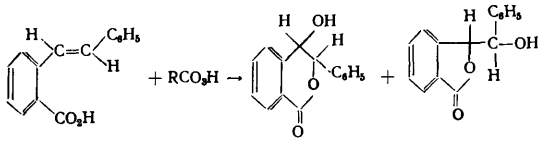
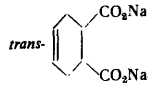
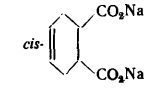
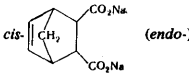
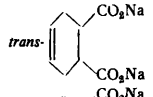
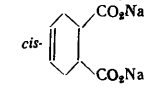
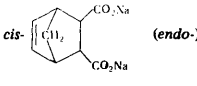


Table 2. Composition of the halogenation products of the sodium salts of unsaturated carboxylic acids in aqueous solutions at 25 °C (according to the data of Staninets et al.[96]).

Halogenating agent and unsaturated acid salt	Yield, %		
	halogeno-lactone	dihalide	halogeno-hydrin
Br, Br_2			
CH_2=CHCH$_2$CH$_2$CO$_2$Na	38	4	58
CH_2=CHCH$_2$CH$_2$CH$_2$CO$_2$Na	19	5	76
CH_2=CHCH$_2$OCH$_2$CO$_2$Na	7	8	85
trans-C_6H_5CH=CHCH=CHCO$_2$Na	0	8	92
trans- 	23	3	74
cis- 	64	3	33
cis-  (*endo*-)	86	7	7
Cl, Cl_2			
trans- 	5	4	91
cis- 	45	—	55
cis-  (*endo*-)	83	8	9

Under the influence of peracids, unsaturated polycyclic carboxylic acids and *o*-allylphenol also participate in AC reactions[102-106].

IV. KINETICS OF ADDITION REACTIONS WITH CYCLISATION

Among AC reactions, the kinetics of iodocyclisation have been investigated in greatest detail. This reaction is very convenient for kinetic studies because it occurs at a measurable and readily controlled rate, is not accompanied by side reactions, and its rate can be readily followed by measuring the decrease in the iodine titre.

The rate of AC reactions with bromine and chlorine are usually too high for measurements by the usual kinetic methods and, moreover, they are accompanied by addition and substitution side processes.

The qualitative kinetic characteristics of iodocyclisation were obtained comparatively long ago. In 1960 de Moura Campos published a series of studies on the rates of iodination of alkyl- and allyl-substituted allylacetic acids [83,107]. However, these were preliminary investigations.

The kinetics of the iodocyclisation of unsaturated compounds of different structures and containing electron-donating groups have been investigated very thoroughly by Shilov and coworkers [15,49,58-61,62,75-77,108-112]. These kinetic measurements were made largely in aqueous solutions.

It was established that all the iodocyclisation reactions investigated obey the simple equation for second-order processes:

$$-\frac{d[I]}{dt} = k[M][I_2] \ ,$$

where [M] is the concentration of the unsaturated compound in its active form, (I) is the analytical concentration of iodine, and $[I_2]$ is the concentration of molecular iodine not bound in the complex I_3^-.

Table 3. The rate constants $k_{20°}$, activation energies $\Delta E^{\neq}$, and the logarithms of the pre-exponential factor $\lg A$ for the iodolactonisation of acid anions with a single multiple bond [15].

Substrate	$k_{20°}$, litre mole^{-1} s^{-1}	$\Delta E^{\neq}$, kcal mole^{-1}	$\lg A$
(I) $CH_2{=}CHCO_2^-$	0	—	—
(II) $CH_3CH{=}CHCO_2^-$	0	—	—
(III) $CH_3{=}CHCH_2CO_2^-$	(0.01)	21	14
(IV) $CH_2{=}CH(CH_2)_2CO_2^-$	84	13.5	11.8
(V) $CH_2{=}CH(CH_2)_3CO_2^-$	10.9	13.2	10.9
(VI) $CH_2{=}CH(CH_2)_4CO_2^-$	0.17	13.2	9.1
(VII) $CH_2{=}CH(CH_2)_5CO_2^-$	0	—	—
(VIII) $CH_3CH{=}CHCH_2CH_2CO_2^-$	142	12.3	12.3
(IX) $C_6H_5CH{=}CHCH_2CH_2CO_2^-$	61	14.8	12.8
(X) o-$CH_2{=}CHC_6H_4CO_2^-$	3.1	16.4	13
(XI) o-$CH_3CH{=}CHC_6H_4CO_2^-$	5.3	16.3	13
(XII) $CH_2{=}CHCH_2CH(CO_2)_2^-$	169	13.5	12
(XIII) $CH{\equiv}C(CH_2)_2CO_2^-$	1.2	14.1	11
(XIV) $CH{\equiv}CCH_2CH(CO_2)_2^-$	3.6	13.9	10
(XV) $CHCl{=}CH(CH_2)_3CO_2^-$	0.025	17.2	11

The constant k depends on the structure, configuration, and conformation of the molecule cyclised, on the reactivity of the multiple bond in relation to electrophilic agents, and on the nucleophilic properties of the electron-donating group D.

Table 3 demonstrates the effect of structural factors in the iodocyclisation of unsaturated carboxylic acid anions‡ in aqueous potassium iodide solutions. It shows that the tendency towards iodocyclisation is shown almost exclusively by compounds with a structure which can give rise to five- and six-membered rings. The formation of the seven-membered iodolactone (VI) is already 70 times slower than that of the six-membered lactone (V) and the rate of formation of rings with more than seven members or less than five members is virtually zero.

The replacement of a hydrogen atom at the extreme carbon atom in the $CH_2{=}CH$-group by an alkyl group appreciably accelerates the iodination [compounds(IV)–(VIII)], while substitution in C_6H_5 has only a slight effect [compound (IX)]. When the benzene ring is incorporated in the chain undergoing closure, the reaction is greatly retarded [compounds (X) and (XI)]. A chlorine located at the double bond also greatly retards the reaction [compound (XV)].

Table 4. The rate constants $k_{20°}$, activation energies $\Delta E^{\neq}$, and the logarithms of the pre-exponential factor $\lg A$ for the iodolactonisation of the anions of alkenoic and alkadienoic acids [112].

Iodinated anion	$k_{20°}$, litre mole^{-1} s^{-1}	$\Delta E^{\neq}$, kcal mole^{-1}	$\lg A$
$CH_2{=}CHCH{=}CHCO_2^-$	0.034	18.5	15.3
$CH_2{=}CHCH_2CH_2CO_2^-$	84	13.5	12.0
$CH_3CH{=}CHCH{=}CHCO_2^-$ (*trans, trans*)	0.062	17.2	14.6
$CH_3CH{=}CHCH{=}CHCO_2^-$ (*trans, cis*)	6.6	14.0	11.1
$CH_3CH{=}CHCH_2CH_2CO_2^-$	142	12.3	12.3
$C_6H_5CH{=}CHCH{=}CHCO_2^-$	0.027	20	15.4
$C_6H_5CH{=}CHCH_2CH_2CO_2^-$	61	14.8	12.8
$CH_2{=}CHCH{=}CHCH_2CO_2^-$	0.95	16.2	12.1
$CH_2{=}CHCH_2CH_2CH_2CO_2^-$	12	13.6	11.1

The experimental data in Table 4 make it possible to estimate the effects of conjugated double bonds on reactivity. Comparison of the rate constants k for the iodocyclisation of acids with a single double bond in Table 3 with the rate constants for the reactions of compounds with analogous structures listed in Table 4 shows that the compounds containing conjugated double bonds are less active by approximately three powers of 10 than their non-conjugated analogues. This retardation is associated with the increase of activation energy. The compensation by the entropy factor is insufficient.

In a series of studies [19,109-111] the changes in reactivity with increase of the rigidity of the molecular structure were investigated. The mono- and di-anions of Δ^4-tetrahydrophthalic acids (I) and (V) and their bridged derivatives (II)–(VII) were iodinated under identical conditions (Table 5).

In almost all cases the reaction leads to the formation of a five-membered iodolactone. The dianion of unsubstituted tetrahydrophthalic acid is iodinated 50 times faster than the monoanion but more slowly than the allylacetate anion (Table 2). When the molecule contains an *endo*-ethylene group [compounds (II) and (VI)], the rate of iodination of the monoanion is 85 times higher than that of its analogue without an inner bond. If the molecule contains a methylene bridge [compounds (III) and (IV)], the rate of iodination increases very greatly: by 4 powers of 10 for the *trans*-isomer and even more for the *cis*-derivative.

We may note that the activation energies in iodolactonisation reactions of monoanions for compounds with a

‡ With the exception of α-alkyl-substituted allylacetate ions discussed in a separate section below.

methylene bridge are lower by 3 kcal mole^{-1} than for the monoanions of compounds without a bridge or with an *endo*-ethylene bridge. The activation energy falls to the same extent on passing from monoanions to dianions [compounds (I)–(V) and (II)–(VI) in Table 5].

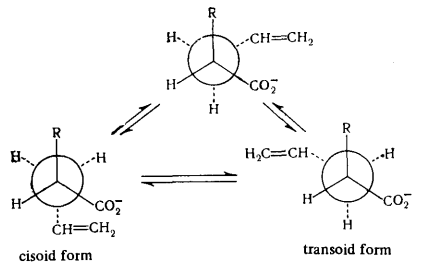
The increase of the rate of iodocyclisation is caused both by the decrease of $\Delta E^{\neq}$ and the increase of the entropy of activation. Consequently there is no "compensation effect" in these systems.

Table 5. Kinetic data for the iodolactonisation of Δ^4-tetrahydrophthalate anions and their bridged derivatives [110].

Compound iodinated	Reaction rate constant $k_{20°}$, litre mole^{-1} s^{-1}	Activation energy $\Delta E^{\neq}$, kcal mole^{-1}	Activation entropy $\Delta S^{\neq}$, e.u.
Acid monoanions			
(I) *cis*-Δ^4-Tetrahydrophthalate	0.4	13.8	24.5
(II) *cis*-3,6-*endo*-Ethylene-Δ^4-tetrahydrophthalate	34	13.7	15.8
(III) *trans*-3,6-*endo*-Methylene-Δ^4-tetrahydrophthalate	4340	10.6	7.6
(IV) *cis*-3,6-*endo*-Methylene-Δ^4-tetrahydrophthalate	15 200	10.9	4.2
Acid dianions			
(V) *cis*-Δ^4-Tetrahydrophthalate	21	10.6	18.4
(VI) *cis*-3,6-*endo*-Ethylene-Δ^4-tetrahydrophthalate	350	10.8	11.8
(VII) 3,6-*exo*-Methylene-Δ^4-tetrahydrophthalate	0	-	-

The *exo*-isomer (VII) is not iodinated at all, which can be readily accounted for by the steric hindrance at the carboxylate ion due to the bridge.

A relation between the rate of iodolactonisation and the proportions of the conformers of the compounds has been established for the anions of α-alkyl-ω-pentenoic acids. These acids exist in cisoid and transoid forms, between which an equilibrium is established, whose position depends on the structure of the compound:



cisoid form transoid form

The constants for the equilibrium between the conformers were calculated using an additive method [112]. The rates of iodolactonisation were measured in the usual way for a number of acids [111]. The results of the kinetic measurements and calculations are presented in Table 6.

Evidently the introduction of an alkyl group in the α-position of allylacetic acid increases the rate of iodination and to a greater extent the more branched is the group. This acceleration corresponds to the content of the *cisoid* conformer in the equilibrium mixture. If the iodination rate constant is referred to the content of the *cisoid* conformer, the calculated values of k_{cis} are found to be constant for all the acids investigated.

Evidently the anions of unsaturated carboxylic acids are iodolactonised only in the cisoid form.

The study of the kinetics of the iodocyclisation of compounds with a heteroatom Δ = O, S, or NH in the unsaturated chain showed that the replacement of a CH_2 group by O, S, or NH retards the reaction (Table 7). [57,59]

Table 6. Dependence of the rate constant for the iodolactonisation of α-R-allylacetate anions on the concentration of their cisoid conformers.

R	$k_{20°}$, litre mole^{-1} s^{-1}	Cisoid conformer, %	$10^{-3}k_{cis}$, litre mole^{-1} s^{-1}
H	84	7	1.21
CH_3	420	35	1.20
C_2H_5	500	40	1.25
n-C_3H_7	500	40	1.25
CH_2=$CHCH_2$	440	40	1.10
n-C_4H_9	560	46	1.22
i-C_3H_7	940	75	1.25
sec.-C_4H_9	980	80	1.28
tert.-C_4H_9	1340	88	1.37
		Mean	1.2

Shilov and Tsegel'nyuk [59] explained these changes in reactivity by the lowering of the mobility of the chain undergoing ring closure in the series O < S < NH < CH_2. The absolute values of k and $\Delta E^{\neq}$ naturally depend also on the electronic effects of the heteroatom.

Table 7. Rate constants and activation energies for the iodocyclisation of compounds with the structure [59]

$$CH_2{=}CHCH_2{-}\Delta{-}CH_2CO_2^-.$$

Δ	$k_{30°}$, litre mole^{-1} s^{-1}	$\Delta E^{\neq}$, kcal mole^{-1}	lg$A$	$\Delta S^{\neq}$
O	0.14	14.5	8.63	−3.28
S	0.45	15.8	11.1	−9.79
NH	6.98	17.1	14.3	+4.58
CH_2	22.4	13.1	10.0	−10.9

The most important characteristic of the electron-donating group in the kinetics of AC reactions is its nucleophilicity. This relation can be followed in a series of kinetic experiments on the iodination of unsaturated compounds the chain structure of which remains unchanged and only the component D is varied [15,61,75,77].

Table 8 presents the results of the measurements of the rate constants for iodocyclisation in a group of unsaturated compounds, which leads to the formation of five-membered heterocycles.

Table 9 presents data on the kinetics of the iodination of substituted 2-allylphenols via the mechanism

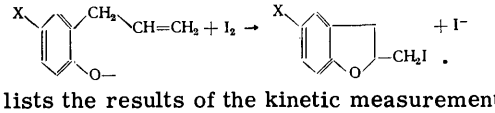


Table 10 lists the results of the kinetic measurements for the iodocyclisation of unsaturated compounds in which the electron-donating groups differ markedly not only in basicity but also in chemical structure. Tables 8–10 list

the pK_a values for the compounds undergoing iodocyclisation as the characteristics of their nucleophilic properties. Evidently the reactivity of the molecules increases with the pK_a.

While the weakly basic SO_3^- group in butene-ω-sulphonate does not participate in the iodocyclisation reaction, the rate constants for the iodination of the strongly basic ω-pentenylamines reach values of 10^5 litre $mole^{-1}$ s^{-1}. For substituted allylphenols, where the variation of basicity is not so great (Table 9), the correlation between the iodocyclisation rate constants and the pK_a is described by the Hammett equation.

Table 8. Rate constants for the iodination of the ω-butenyl derivative[15]

$CH_2=CHCH_2CH_2-R.$

R	$k_{20°}$, litre $mole^{-1}$ s^{-1}	$\Delta E^{\neq}$, kcal $mole^{-1}$	lgA	pK_a
SO_3^-	0	—	—	—
CH_2SCH_3	0.003	17.3	8.0	—
$CONH_2$	0.67	12.2	8.9	−0.4
CH_2OH	1.47	8.9	7.8	—
CH_2NH_2	$1.4\cdot10^5$	2.8	7.2	10.5
CH_2NHCH_3	$2.3\cdot10^5$	1.6	6.7	10.1
$CH_2N(CH_3)_2$	$1.8\cdot10^5$	1.9	7.2	10.3

At the same time comparison of the above tables shows that some of the compounds iodinated have the same or similar pK_a's but the rates of their cyclisation differ markedly. This is not surprising, since the rate of AC reactions does not depend on the basicity of the D component alone.

Other factors which determine the reactivity of the electron-donating component of unsaturated compounds in AC reactions are polarisation, steric, etc. factors which characterise its intrinsic nucleophilicity.

Table 9. Rate constants for the iodination of the ions of X-2-allylphenols[77].

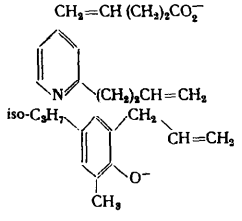
X	$k_{20°}$, litre $mole^{-1}$ s^{-1}	$\Delta E^{\neq}$, kcal $mole^{-1}$	lgA	pK_a
4-Nitro	46	5.2	5.5	7.1
4-Phenylazo	80	5.0	5.5	7.4
4,6-Dichloro	170	3.2	4.6	8.5
4-Chloro	176	3.8	5.3	9.3
4-Bromo	180	4.0	5.5	9.4
4-Methyl	360	3.4	5.2	10.1
4-Methoxy	420	3.2	5.1	10.3

Tables 8 and 9 show that, for the same or similar reaction series, the observed variation of the iodocyclisation rate constant depend mainly on the activation energy, since the activation entropy and the corresponding frequency factors are fairly constant, particularly for allylphenols. For a given reaction series, the relation between the cyclisation rate constant and the nucleophilicity of the electron-donating component is expressed in the fact that the more nucleophilic is the electron-donating component of the unsaturated molecule, the higher is the rate constant and the lower the activation energy.

In the cyclisation of unsaturated compounds the electron-donating components of which differ greatly in chemical structure (Table 10), this relation is less distinct.

Analogous kinetic relations are observed also in the chloromercuration of 2-allylphenols and unsaturated alcohols[97,98]. Phenoxide anions are more reactive in these processes by three powers of 10 than the free phenols.

Table 10. Activation parameters and rate constants for AC reactions.

Compound iodinated	$k_{20°}$, litre $mole^{-1}$ s^{-1}	$\Delta E^{\neq}$, kcal $mole^{-1}$	$\Delta S^{\neq}$, e.u.	lgA	pK_a	Refs.
$CH_2=CH(CH_2)_2CO_2^-$	84	13.5	−5.58	11.2	4.68	15
	173	7.2	−23.7	7.8	8.03	75
	7770	1.7	−35.8	5.1	10.1	77

Interesting experimental data have been obtained, which make it possible to compare the rates of chloromercuration in AC reaction and non-cyclic addition reactions. It has been established that the rate constant k for chloromercuration at 25°C by $HgCl_2$ is 450 times higher for pent-1-en-5-ol than for its methyl ether[98].

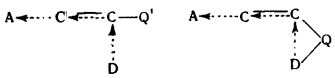
V. THEORETICAL DISCUSSION OF ADDITION REACTIONS WITH CYCLISATION

AC reactions are a variety of addition reactions of a general type involving, apart from the unsaturated molecule, electron-accepting and electron-donating agents, the transition state of which may be described by the scheme D → M → A.[113-115] A characteristic feature of AC reactions is that the nucleophilic component D is linked by a valence bond to the M molecule and therefore the reaction is bimolecular in relation to the addition of the electrophilic agent and intramolecular in relation to the nucleophilic agent§.

§ Previously it was postulated (see, for example, Refs. 6 and 13) that the formation of a ring in addition reactions takes place in two consecutive stages: the product of direct addition of the electrophilic agent to the multiple bond is formed initially and then ring closure takes place as a result of an exchange reaction between the added atom and the electron-donating end of the molecule.

Linstead and May[19] were the first to point out that the mechanism involving simultaneous addition and ring closure is more likely. It is not difficult to demonstrate that the hypothesis of a general two-stage exchange cyclisation mechanism is erroneous. In fact in many cases analogous intermolecular reactions involving addition to multiple bonds do not occur at all and, when direct addition products can be observed (for example, vicinal dibromo-substituted acids), they prove to be stable and their cyclisation is much slower than the corresponding AC reaction. In particular, certain characteristics of chloromercury-cyclisation suggest this hypothesis[69,97,98]. Such reactions evidently cannot be included in the category of AC reactions.

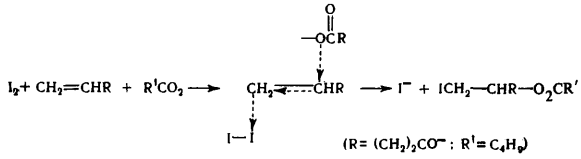
This difference between the transition states can be represented by the scheme



intermolecular reaction AC reaction

As a result of the intramolecular addition mechanism, AC reactions (in which five- or six-membered rings may be formed) sometimes take place much faster than the analogous trimolecular reactions[114-116]¶.

The addition reactions occurring under the influence of weak electrophilic agents, in particular iodine, are especially instructive in this respect. In many such cases trimolecular addition reactions do not occur at all. For example, as already noted, the allylacetate ion readily forms 5-iodo-4-valerolactone under the influence of iodine in aqueous potassium iodide solution. This reaction would correspond to a trimolecular mixed compound involving the anion of allylacetic or other carboxylic acid formed via the mechanism



$(R = (CH_2)_2CO^-;\ R' = C_4H_9)$

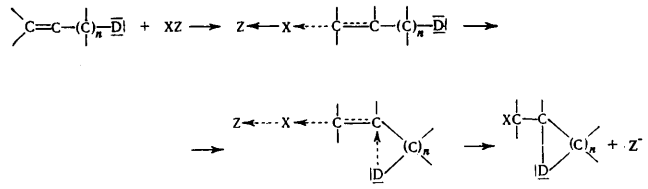
However, even at high concentration of the added anions, for example butyrate anions, this type of reaction does not occur and the rate of iodocyclisation does not change[67].

Competition between cyclic and non-cyclic addition takes place when the reactivity of the ring-closure group is reduced[57] or when more vigorous electrophilic agents are employed, as shown above for bromination and chlorination.

Another characteristic feature of AC reactions is that they are much more sensitive to the nucleophilic properties of the electron-donating component than non-cyclic addition reactions[114,115]. We have seen that the rate constant for iodocyclisation can change by many powers of 10 as the nucleophilic properties of the D component are altered. In reactions involving mixed trimolecular additions, this type of relation is much weaker or is altogether absent. For example, there are data for the rates of chlorination of olefins in the presence of various electron-donating agents in acetic acid[119,120]. The increase of the rate of these reactions is proportional to the concentration of donors in the mixture but a definite relation between the rate constant and the nucleophilicity of the anion is not found.

When allyl alcohol is iodinated, the effect of the nucleophilic properties of the electron-donating agent is appreciable but is nevertheless inferior to that observed in iodocyclisation reactions[121,122].

The above characteristics of AC reactions indicate the particular importance of nucleophilic attack in such processes, in contrast to noncyclic addition reactions. In AC reactions the electron-donating group evidently reacts with the primary weakly polarised complex formed by the electrophilic agent molecule with the multiple bond. The reaction occurs as a synchronous process in which the complex bond is converted into a valence bond and ring closure takes place:



The synchronous effect of the electron-accepting and electron-donating groups on the multiple bond in the molecules in AC reactions can appreciably lower their activation energy. AC reactions proceed with negative activation entropies, the absolute values of which fall from several tens to several entropy units for unsaturated compounds with rigidly fixed reaction centres[49].

The presence in one molecule of two reaction centres (the C=C bond and the electron-donating group) capable of interacting synchronously with the electrophilic agent is also favourable from the standpoint of the entropy change, since such reaction requires a relatively lower structural rearrangement in the reaction system than, for example, in intermolecular acyclic addition.

Acyclic trimolecular addition of iodine occurs only in the presence of powerful nucleophilic agents in view of the weak polarisation by iodine of the multiple bond in the π complex. Weak nucleophilic agents cannot interact effectively with the multiple bond of the weakly polarised π complex of iodine.

If, however, a powerful electrophilic agent, for example bromine, is involved in the intermolecular reaction, a highly polarised complex (probably an ion pair or a σ complex) is formed and is so active that the nucleophilic cooperation of the electron-donating component loses its importance to a considerable degree[96]. AC reactions can also proceed via a σ-complex but only in competition with non-cyclic addition. Although non-cyclic bromination reactions are somewhat accelerated by nucleophilic agents, the nucleophilic properties of strong acid anions are sufficient to complete the addition.

The role of nucleophilic cooperation in AC reactions increases when there is a possibility of the formation of five- and six-membered rings. In the case of small rings (three- and four-membered) there is no nucleophilic cooperation or it is hindered by virtue of certain steric effects. For larger rings, there is a decrease of the probability of a favourable disposition of the multiple bond and the electron-donating end of the molecule as a result of the increase of the number of conformations which the reacting molecule may assume.

These factors operate also in many other chemical reactions, promoting the formation of five- and six-membered rings. In this respect AC reactions constitute a special case obeying the general principle.

As a favourable disposition of the reaction centres—the double bond and the electron-donating group D—is more firmly fixed in the unsaturated molecule M, the AC reaction is facilitated to a greater extent. Therefore in very rigid systems, for example the anions of *endo*-methylenetetrahydrophthalic acids, high rates of ring closure are observed. Conversely, the more mobile is the chain of the reacting molecule, the slower is the AC reaction[49,57,110]. These relations are reflected to some degree in the parameters of the Arrhenius equation when similar series of compounds are considered.

¶ This ease of formation of five- and six-membered rings serves as a confirmation of the old idea that cyclic transition complexes play a major role in heterolytic reactions[117,118].

Thus we find that the differences between the rates of iodination in the series of acid anions with the structure $CH_2=CH(CH_2)_nCO_2^-$ are related to the changes in activation entropy, while the values of $E^{\neq}$ are fairly close (Table 3). Conversely the dependence of the rate of reaction on the nucleophilic properties of D is related to the activation energy and only to a lesser extent to the activation entropy. The acceleration of AC reactions for rigid *endo*-methylene and *endo*-ethylene systems depends both on the lowering of $E^{\neq}$ and the increase of entropy (Table 5). Examination of a large number of the thermodynamic parameters of activation of AC reactions reveals a superposition of various electronic and steric effects, which hinder the isolation of a particular factor in a pure form.

In particular, one can show that the presence of a methylene bridge, which makes the molecule very rigid, is associated with a considerable strain of the double bond, which is estimated as 6 kcal mole^{-1} relative to the unstrained double bond in the cyclohexene ring or the double bond in the same ring with an internal *endo*-ethylene bridge[123]. Thus in AC reactions of molecules with methylene bridges there is, in addition to the steric effect, also the electronic effect associated with the double bond strain. We may note that the products of AC reactions are thermally and chemically more stable than the analogous non-cyclic adducts.

The importance of the formation of five-, six-, and seven-membered active complexes in organic reactions was discussed by Syrkin 10 years ago[124]. He put forward the idea that the electronic perturbations in these processes entail a lowering of the activation energy owing to the formation of more stable quasi-aromatic systems. The idea of the aromaticity of the cyclic complex apparently was not developed further and its applications have been by no means always correct. However, the general assertion of "a kind of parallelism between thermodynamics and kinetics" in chemical reactions is probably valid.

It appears that in AC reactions we have a kind of combination of steric and energetic conditions whereby the electron-donating group is maintained in contact with the polarised atom of the multiple bond. The active electron-donating atom remains at the multiple bond for a longer period than in trimolecular reactions and this corresponds to a lowering of the chemical potential necessary for the formation of stable reaction products.

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Thermostable Polymers from Dianhydrides of Aromatic Tetracarboxylic Acids and Tetra-amines

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The preparation, properties, and structure of polymers based on dianhydrides of aromatic tetracarboxylic acids and tetra-amines are surveyed. Compounds of this type possess excellent thermal stability, resistance to radiation and chemicals, catalytic activity, and semiconductor properties. The fields of practical application of the polymers are examined. A list of 77 references is included.

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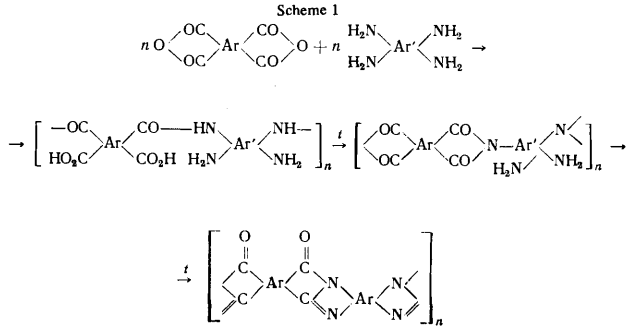
I. INTRODUCTION

At the present time much attention is paid to the synthesis and investigation of thermostable polymers [1]. This has arisen from the demands made by rapid developments in technology—especially such advanced fields as aircraft and spacecraft construction, nuclear power, and electrical technology—for materials capable of operating under severe conditions of high-temperature gas flows and radiation. During recent years progress has been made in producing a series of polymers having a conjugated system comprising various carbocyclic and heterocyclic rings in a macromolecular chain of ladder and block–ladder structure.

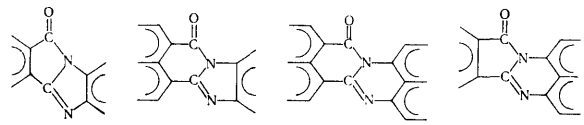
Considerable interest attaches in this series to macromolecular products of the reaction of dianhydrides of aromatic tetracarboxylic acids and tetra-amines (Scheme 1):

Scheme 1



They are polymeric analogues of the highly stable aroylenebenzimidazole dyes [2].

The repeating unit in the macromolecular chains includes a system of fused aromatic carbocyclic and heterocyclic rings



Depending on the type of heterocycles formed in the process the polymers have been termed polyimidazopyrrolones (pyrrones), polyaroylenebisbenzimidazoles or polyaroylenebenzimidazoles, polyperimidinetetrayls, polybisbenzimidazophenanthrolines, etc. In principle none of these names completely represents the structure of the polymers, especially when intermediate groups and complicated fused carbocyclic and heterocyclic rings are present. The Reviewers therefore consider it advisable to use the trivial, but already quite widely employed name "pyrrones" with an indication of the initial components, and only in isolated cases to retain the names of the polymers given in the original papers. The first work on the synthesis of polymers of this class was published in 1965–1966. [3-8] At the present time the preparation and properties of pyrrones are being actively investigated, and these compounds may be expected to find wide application in the immediate future.

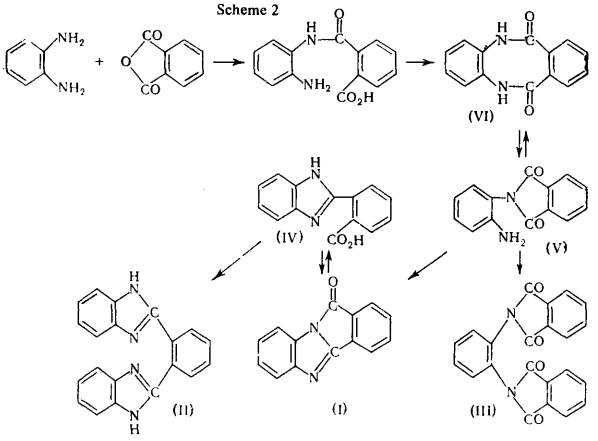
II. REACTION BETWEEN AROMATIC ANHYDRIDES AND *o*-DIAMINES

In the reaction between aromatic dianhydrides and tetra-amines, the formation of the final polymers is preceded by that of several intermediate structures. In

order to elucidate the mechanism of polycondensation, therefore, it is advisable to examine papers on the interaction between aromatic *ortho*- or *peri*-diamines and anhydrides.

Possible reactions in the condensation of phthalic anhydride with *o*-phenylenediamine can be represented by Scheme 2:

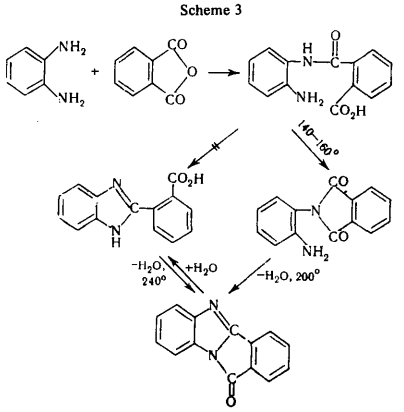
Scheme 2



The reaction products have been described in several papers[2,3,8-10]: depending on the conditions 1,2-benzoylenebenzimidazole (I), *o*-phenylenedibenzimidazole (II), *NN'*-diphthaloyl-*o*-phenylenediamine (III), *o*-benzimidazol-2'-ylbenzoic acid (IV), and *N*-*o*'-aminophenylphthalimide (V) have been isolated. Stetter[11] obtained a substance containing an eight-membered ring (VI) by reaction between phthaloyl chloride and *o*-phenylenediamine. Porai-Koshits and Antoshul'skaya[12] obtained the compounds (II)–(V) by fusing the components in various proportions, and established that compound (III) is formed with the greatest difficulty, whereas (II) and (IV), which contain imidazole rings, are formed more readily. Arient and Marhan found[13] that small quantities of (V) and (VII) are formed initially in methanol at moderate temperatures. At the boiling point only (V) is present in the mixture initially, and the imidazole derivative (IV) is formed. On further heating the composition of the mixture remains almost unchanged: the product contains the two compounds in the approximate proportions 1 : 1.

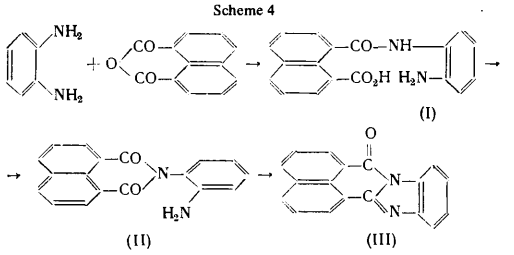
Dawans and Marvel[4] used nuclear magnetic resonance to investigate the products obtained by conducting the reaction in dimethyl sulphoxide: the n.m.r. spectra indicated the presence of a mixture of the final products. It was assumed[4] that competitive formation of the acid (IV) and the amine (V) takes place, one or other product predominating according to the reaction conditions. Colson et al. established[8] that only the amino-imide (V) is formed when *o*-phenylenediamine is heated with phthalic anhydride at 140–160°C for 30 min. Heating this product to 100°C converted it into benzoylbenzimidazole. The latter cannot be formed from the acid (IV) below 240 to 250°C, which is additional evidence for the scheme of cyclisation given by Colson and his coworkers (Scheme 3).

Scheme 3



These results are consistent with those given by Arient[2] showing that *o*-benzimidazolylbenzoic acid is formed only by hydrolysis of 1,2-benzoylenebenzimidazole. If the process takes place in anhydrous medium (in acetic anhydride or in the melt), the reaction halts at the first stage.

Scheme 4



Naphthalic acid reacts with *o*-phenylenediamine in various solvents at temperatures up to 60°C with gradual formation of the amide (I) and from it *N*-*o*-aminophenylnaphthalimide (II). In all cases the final reaction products are the imide (II) and a small quantity of 1,2-naphthoylenebenzimidazole (III).[14] The compound (III) was obtained at higher temperatures. The reaction goes very easily and in quantitative yield[15-17]. 1,2-Naphthoylenebenzimidazole is more stable than 1,2-benzoylenebenzimidazole on prolonged boiling in acid and in alkaline medium. As a consequence, reaction between *o*-phenylenediamine and naphthalic acid ceases at the stage of formation of 1,2-naphthoylenebenzimidazole. On the basis of the above results Scheme 4 has been suggested as the mechanism of the reaction.

Thus it follows from the above results that condensation of aromatic dianhydrides with tetra-amines in anhydrous medium takes place in three successive stages—formation of an amide–amino-acid, cyclisation of the latter to an amino-imide†, and finally conversion of this product into an aroylenebenzimidazole.

†It has been shown recently[18] that the amino-amide is not formed in the reaction of 1,8-naphthylenediamine with phthalic anhydride.

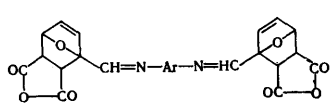
III. SYNTHESIS OF THE POLYMERS

Pyrrones were synthesised by Bell and Pezdirtz [3], Dawans and Marvel [4], the present Reviewers [5], and several other investigators [6-8] almost simultaneously and independently of each other. They used dianhydrides of various *ortho*- and *peri*-tetracarboxylic acids and various tetra-amines (Table 1). In isolated cases the dianhydrides were replaced by the more reactive symmetrical dimethyl dichlorocarbonyl-dicarboxylates, and the stable tetrahydrochlorides have been used instead of readily oxidised tetra-amines.

Table 1. Initial tetra-amines and dianhydrides for the synthesis of pyrrones.

Component	Abbreviation	References
Tetra-amines		
Benzene-1,2,4,5-tetra-amine	BTA	3,4,19-22
Biphenyl-3,3′,4,4′-tetra-amine	BPTA	3,4,5,7,8,19,21, 24-34
4,4′-Oxydiphenylene-1,1′,2,2′-tetra-amine	ODPTA	3,4,8,19,28,31, 34-38
Diphenylmethane-3,3′,4,4′-tetra-amine	DPMTA	19,28,31-34,39
Naphthalene-1,4,5,8-tetra-amine	NTA	4,21,22,40
Benzophenone-3,3′,4,4′-tetra-amine	BOTA	41
p-Phenylenedioxy-4,4′-diphenylene-1,1′,2,2′-tetra-amine	PDODPTA	34;38
Dianhydrides of tetracarboxylic acids		
Pyromellitic	PMDA	3,4,7,8,19,23,27-29, 33,38,39,42-44
Biphenyl-3,3′,4,4′-tetracarboxylic	BPDA	32
4,4′-Oxydiphenylene-1,1′,2,2′-tetracarboxylic	ODPDA	7,34
Benzophenone-3,3′,4,4′-tetracarboxylic	BODA	3,19,28,34,41
Naphthalene-1,4,5,8-tetracarboxylic	NDA	5,20,24-26,31,33, 35,36,40,42,43
Perylene-3,4,9,10-tetracarboxylic	PTDA	5,7,25,31,37
2,8′:2′,8-Dioxy-1,1′-binaphthyl-4,4′,5,5′-tetra-carboxylic	DOBNDA	45

Polymers have been synthesised from dianhydrides of alicyclic tetracarboxylic acids—those of bicyclo[4,2,2]-decane-2,3,7,9-tetracarboxylic acid and its 9-methyl derivative, butane-1,2,3,4-tetracarboxylic acid, and cyclopentane-1,2,3,4-tetracarboxylic acid [33]—and also from hitherto unreported dianhydrides having the structure [26,37,46]



and several others [34].

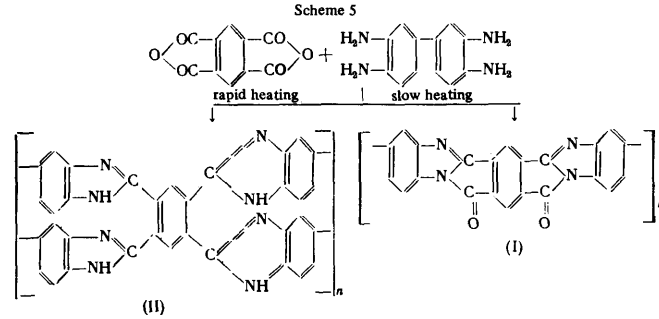
Tetra-amines with spiran structures have also been used for the synthesis [42,43].

Pyrrones have been obtained by conducting the polycondensation in the melt, in the solid phase, and in solution. Two-stage and one-stage methods of synthesis in solution have become most widely used.

1. Polycondensation in the Melt and in the Solid Phase

Polymers have been synthesised from molten pyromellitic dianhydride and various tetra-amines [4]. The mixture of dianhydride and tetra-amine was heated in nitrogen, the temperature being raised gradually to 220°C, and then in a high vacuum at 300–330°C for a few hours. The resulting polymers had predominantly the linear structure (I) (Scheme 5). They were soluble in formic and concentrated sulphuric acids, but in most cases they were insoluble in organic solvents. Their intrinsic viscosity was 0.2–0.5 dl g^{-1}. A rapid rise in temperature during synthesis yields predominantly polymers with network structure (II).

Scheme 5



(II) (I)

Polymers of high molecular weight are formed when the initial reactants are present in equimolecular proportions. Excess of the anhydride increases the yield of polymer (I), but its molecular weight is lower. In most cases the elementary composition of the polymers was consistent with the suggested structure. In order to promote intramolecular cyclisation Dawans and Marvel [4] attempted to dehydrate non-cyclised polymers at low temperatures in the presence of sulphuric acid or acetic anhydride. However, heating with sulphuric acid produced partial sulphonation of the polymer; and in the presence of acetic anhydride (pure or diluted in pyridine) these workers observed acetylation instead of dehydration.

Polymers have been obtained by polycondensation in the solid phase of naphthalene-1,4,5,8-tetracarboxylic dianhydride and biphenyl-3,3′,4,4′-tetra-amine. A mixture of the starting materials was heated under slight applied pressure of nitrogen at 285–295°C for 4 h. The reaction products were cooled in an atmosphere of nitrogen, and dissolved in concentrated sulphuric acid. After supercooling, the logarithmic viscosity of the resulting polymer was 0.22 dl g^{-1}.

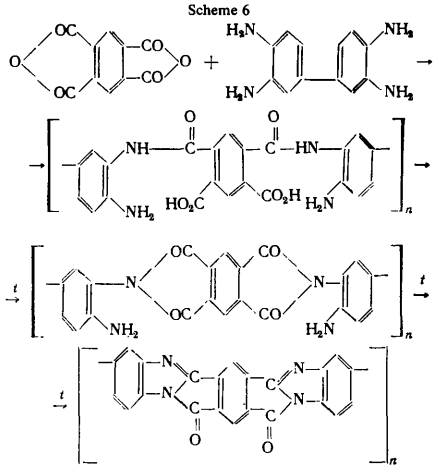
Morgan and Scott [47] have recently proposed a method for preparing polymers of the present type directly at the stage of fabrication into articles. An equimolecular mixture of the dianhydride (of pyromellitic or naphthalene-1,4,5,8-tetracarboxylic acid) and the tetra-amine (biphenyl-3,3′,4,4′-tetra-amine) under high pressure (280 atm) was heated slowly to 450°C in a porous reaction chamber (porous graphite lining). Gaseous and liquid products were driven off under pressure and at a high temperature. The resulting polymers possessed superior mechanical properties and high thermal stability.

2. Polycondensation in Solution

Polycondensation can be conducted in solution in one or two stages. A soluble macromolecular polyamide-amino-acid (PAAA) is obtained in the first stage of the two-stage synthesis. The solvents which have been used are pyridine, dimethyl sulphoxide (DMSO), *NN*-dimethylacetamide (DMAA), *NN*-dimethylformamide (DMFA), 1-methyl-2-oxopyrrolidine [MOP], tetramethylurea, and hexamethylphosphoramide [3-5,31,36,37]. In the second stage the polyamide–amino-acid undergoes polycyclodehydration on heating, with formation of a pyrrone. In the single-stage method the initial reactants are heated to

180–230°C in such solvents as polyphosphoric acid (PPA) or 2,5,8-trioxanonane (diglyme) to yield directly the final polymers.

Scheme 6



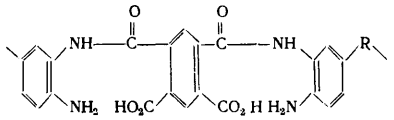
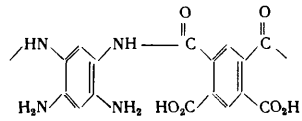
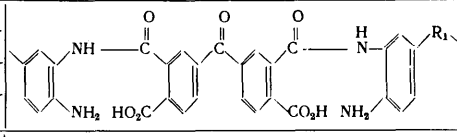
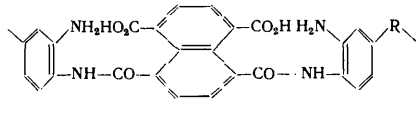
From an investigation of the interaction of model compounds Colson et al.[8] suggested the above sequence of reactions (Scheme 6) in the polycondensation of pyromellitic dianhydride with a tetra-amine.

(*a*) Low-temperature polycondensation—synthesis and properties of polyamide–amino-acids

The first stage in the synthesis of pyrrones—the formation of polyamide–amino-acids—and to a less extent the stage in which polyamino-imides are formed are reversible, so that the molecular weight of the polymers depends on many factors. Low-temperature polycondensation is usually conducted in an aprotic solvent. The optimum reaction temperature depends on the reactivity of the dianhydride used. Acid dianhydrides lie in the sequence—pyromellitic > naphthalene-1,4,5,8-tetracarboxylic > perylene-3,4,9,10-tetracarboxylic— according to their activity in forming polyamide–amino-acids[25,31,36,37]. Such passivation of the dianhydrides in this sequence is due to increasing compensation of the positive charges on the carbon atoms of the anhydride ring by the increasing electron-donating power of the aromatic portion. Polyamide–amino-acids with the highest molecular weights have been obtained from pyromellitic dianhydride at temperatures between −30° and +20°C [27–29,39] and from the naphthalenetetracarboxylic dianhydride at 65–80°C.[24,31,35–37]. The perylenetetracarboxylic dianhydride did not give appreciable yields even when the reactants were heated to 150–160°C. Only on prolonged heating at 170–200°C were partly cyclised polymers obtained[25,31], having composition similar to polyamino-imides (Table 2).

The Reviewers have recently been able to lower considerably the temperature of the first stage by using lithium salts. On investigating the synthesis of polyamide–amino-acids from naphthalenetetracarboxylic dianhydride and the tetra-amine of diphenyl ether they

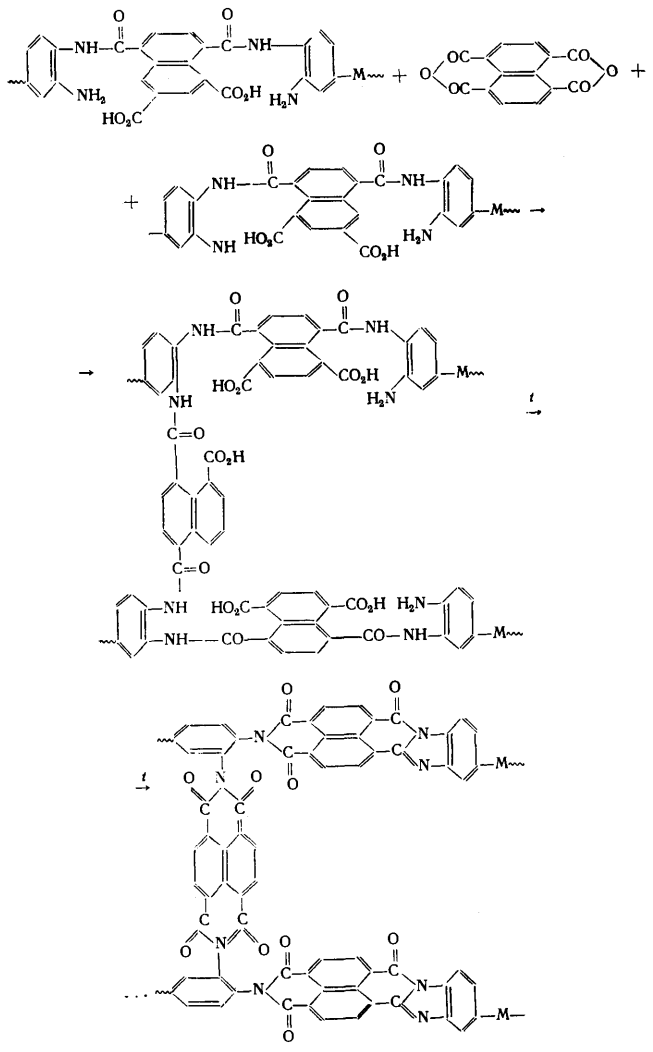
Table 2. Polyamide–amino-acids obtained by low-temperature polycondensation.

Initial components		Repeating unit	Synthesis conditions			Viscosity	Ref.
dianhydride	tetra-amine		R	temp., °C	solvent		
PMDA	BPTA		—	20	DMFA	0.81–0.99[a]	19, 27
	BPTA, 4HCl		—	20	DMAA	0.47[a]	19
	ODPTA		—O—	20	DMFA	0.25[b]	4
				20	DMAA	0.59[a]	19
	DPMTA		$-CH_2-$	20	DMAA	0.74[a]	19
				−20÷+30	DMFA	—	39
Dimethyl 4,6-dichloro-carbonyl-isophthalate	BTA		—	20	DMSO	0.25[c]	8
	BTA, 4HCl		—	20	DMSO	0.77[a]	19
BODA	BPTA		—	20	DMFA	1.45[a]	19
	ODPTA		—O—	20	DMAA	1.11[a]	19
	DPMTA		$-CH_2-$	20	DMAA	0.72[a]	19
	BOTA		—CO—	20	DMFA	0.43[d]	19
NDA	BPTA		—	75	DMSO	0.43[d]	31
	ODPTA		—O—	75	DMSO	0.79[d]	31
				80	DMFA	0.59[r]	
	DPMTA		$-CH_2-$	75	DMSO	0.36[d]	31

[a] Intrinsic viscosity at 25°C in solvent used for synthesis. [b] Specific viscosity of 0.5% solution in formic acid at 20°C. [c] Intrinsic viscosity in DMSO at 30°C. [d] Specific viscosity of 1% solution in DMFA at 25°C.

established[31,36,37] that up to 50°C the viscosity of the reaction solution increases very slowly and does not exceed 0.2 dl g^{-1}, over the range 65–80°C the increase accelerates considerably, and when the temperature is raised to 100°C individual amino-imide fragments are formed as a result of cyclisation in the chain of the polyamide–amino-acids. This sequence and the rate of addition of the reactants have a substantial effect on the rate of increase in the molecular weight of the polyamide–amino-acids.

Scheme 7



The same factors govern the possibility and time of gel formation. With slow addition of a dianhydride to a solution of a tetra-amine the rate of increase in the molecular weight of the polyamide–amino-acids is small, since transamination plays an important role in this case. Gel formation is observed in the later stages of polycondensation[36]. The time to gel formation decreases with increase in the temperature, the rate of increase in molecular weight of the polyamide–amino-acids, and also the local concentration of dianhydride in the solution. Gels are partly soluble in aprotic solvents and to a considerable extent in concentrated sulphuric acid. On prolonged standing they pass into a product which swells but is insoluble in sulphuric acid. The gels differ little in composition from soluble polyamide–amino-acids, and like the latter have an amorphous structure.

High-temperature cyclisation of a gel, in contrast to the soluble polyamide–amino-acids, yields polymers which are insoluble in sulphuric acid[36]. The main reaction in which polyamide–amino-acids are formed can evidently be accompanied by a secondary reaction between the dianhydride and amino-groups in the chain of the resulting polyamide–amino-acid. Although the basicity and hence the reactivity of these groups is low, the probability of their interaction with the dianhydride increases in the later stages of polycondensation, when little free tetra-amine and few reactive terminal amino-groups are present (Scheme 7).

The intensity of transamination and the probability of secondary reactions leading to gel formation depend significantly on the basicity of the tetra-amine and the reactivity of the dianhydride. Thus addition of pyromellitic dianhydride to a solution of a tetra-amine leads in all cases to the formation of a large quantity of gel. When the solutions are mixed in the opposite sequence, the whole of the polymer is instantly precipitated as a gel. When naphthalene-1,4,5,8-tetracarboxylic dianhydride and various tetra-amines are added together, gel formation is observed only after 2–6 h.[31,36]

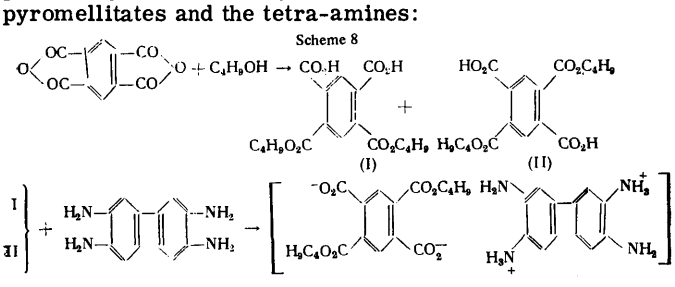
Tetra-amines of low basicity, e.g. bis-3,4-diaminophenyl sulphone, play an active part in transamination. However, their use diminishes the difference in basicity between terminal amino-groups and those in the chain of the polyamide–amino-acids, which favours intermolecular cross-linking of the chains. By using inorganic salts the Reviewers have been able also to vary the optimum conditions for the synthesis of polyamide–amino-acids of high molecular weight and eliminate the possibility of gel formation.

Korshak and his coworkers[39] also observed fairly rapid gel formation at room temperature in the polycondensation of pyromellitic dianhydride with diphenylmethanetetra-amine. A linear product could be obtained by lowering the temperature of the synthesis to between −20° and −30°C. Polycondensation at a high temperature leads to partial imidisation. The temperature at which this latter process begins in an aprotic solvent is determined by the nature of the dianhydride and of the tetra-amine.

Imidisation is accompanied by the separation of a certain amount of water, in whose presence of dianhydride is converted into the less reactive tetracarboxylic acid. A slight (1–2%) excess of the dianhydride is necessary to restore equivalence. Further increase in the excess (above 2%) of pyromellitic dianhydride in the reaction with tetra-amines leads to increased viscosity of the polyamide–amino-acids and rapid gel formation[19]. The synthesis of polyamide–amino-acids from naphthalene-1,4,5,8-tetracarboxylic dianhydride and tetra-amines is characterised by a diminution in viscosity when the excess of dianhydride exceeds 2%.[36] A fall in viscosity is observed also when excess of the tetra-amine is used (Scheme 8).

Bell[48] achieved strict equimolecularity of the components by first obtaining the salts from *m*- or *p*-dialkyl pyromellitates and the tetra-amines:

Scheme 8



Heating these salts in dimethylacetamide gave polymers having predominantly the structure of polyamide–amino-acids. Heating the dry salt in a vacuum or in an inert atmosphere yielded polybenzimidazopyrrolones.

The best solvents for the reaction are dimethylacetamide, dimethyl sulphoxide, and 1-methyl-2-oxopyrrolidine [31,36,37]. The reduced viscosity of polyamide–amino-acids depends on the concentration of the reactants. The presence of moisture in the solvent lowers the viscosity of the resulting precondensates.

Easily oxidisable tetra-amines, e.g. benzene-1,2,4,5-tetra-amine, have been replaced by their stable tetrahydrochlorides for polycondensation with dianhydrides [3,19]. A solution of pyromellitic dianhydride was added over 2–20 h to a suspension of the tetrahydrochloride in the presence of an acceptor for hydrogen chloride. The resulting polymers were identical in structure and properties with those obtained by other methods. Bell and Jewell [19] replaced the dianhydride, which reacts very slowly with tetra-amine tetrahydrochlorides, by dimethyl 4,6-dichlorocarbonylisophthalate. In this case tertiary amines are ineffective as acceptors of hydrogen chloride, while use of the free amine leads to precipitation of the polymer.

Polyamide–amino-acids are coloured (pale yellow to brown) powders soluble in aprotic solvents. Keeping dilute (1–2%) polymer solutions at 20°C decreases the viscosity of the polyamide–amino-acids. A more substantial fall in viscosity occurs in a moist solvent. Gel formation was observed on the prolonged storage of 10% solutions of polyamide–amino-acids (from naphthalene-1,4,5,8-tetracarboxylic dianhydride and 4,4′-oxydiphenylene-1,1′,2,2′-tetra-amine). [36]

Available data on the molecular-weight characteristics of polyamide–amino-acids usually consist merely of an indication of the intrinsic or the reduced viscosity. Osmometric measurements on polymers obtained from pyromellitic dianhydride and certain tetra-amines gave molecular weights of 7000–20 000, while the intrinsic viscosity was 0.4–1.5 dl g^{-1} (in dimethylformamide at 25°C) [19,30].

Most polyamide–amino-acids form strong transparent films when their solutions are evaporated. Polymers having intrinsic viscosity $\geqslant 0.4$ dl g^{-1} are suitable for the preparation of films. The strength of films dried at 125°C (obtained from pyromellitic dianhydride and tetra-amines) is 700–1050 kgf cm^{-2}, their relative elongation 25–35%, and the modulus of elasticity 14 000–28 000 kg cm^{-2}. [29,30] The tensile strength of the polyamide–amino-acid films based on naphthalene-1,4,5,8-tetracarboxylic dianhydride and tetra-amines was 850–950 kgf cm^{-2}. [31,36] These films usually contained 9–12% of solvent.

(*b*) Transformation of polyamide–amino-acids

The conversion of polyamide–amino-acids into pyrrones represents the second stage of polycondensation, and consists in intramolecular polydehydration accompanied by formation of a polyaminoimide and then the final polymer. Polycyclisation is accomplished by heat-treating the polyamide–amino-acid films or powders in a vacuum or in an inert atmosphere, and also by heating their solutions in polyphosphoric acid. Heating involved raising the temperature either smoothly or in steps to 200–400°C and maintaining the polymers at these temperatures.

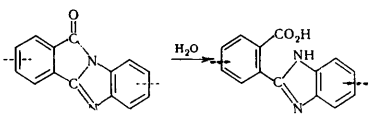
Thermogravimetric analysis proved to be unsuitable for the kinetic study of the polydehydration of films [3,35], since the solvent forms with the polyamide–amino-acid a complex which decomposes at temperatures corresponding to the start of cyclisation of the acid. The thermogravimetric method has been used to investigate the kinetics of the cyclodehydration of various polyamide–amino-acid powders (formed by biphenyl-3,3′,4,4′-tetracarboxylic dianhydride with biphenyl-3,3′,4,4′-tetra-amine, 4,4′-oxydiphenylene-1,1′,2,2′-tetra-amine, and diphenylmethane-3,3′,4,4′-tetra-amine respectively; and by biphenyl-3,3′,4,4′-tetra-amine with the dianhydrides of pyromellitic and naphthalene-1,4,5,8-tetracarboxylic acids). [32,33] Cyclodehydration is found to be of first order [32] and to occur in two stages [33].

Cyclisation has been studied by infrared spectroscopy [3,8,24,31,41,44,50,51]. Polyamide–amino-acids obtained from pyromellitic dianhydride and tetra-amines show characteristic absorption bands due to secondary amides in the region of 1660, 1650, 1540, 1505, 1305, and 1280 cm^{-1}, bands in the region of 1720 and 1605 cm^{-1} due to the presence of carboxy-groups, and bands in the range 3200–3400 cm^{-1} due to amino- and imino-groups. On cyclisation of these acids absorption appears at 1710 and 1720 cm^{-1}, which is characteristic of imide rings, absorption at 1310 cm^{-1} due to the presence of a tertiary nitrogen atom, and a band at 1470 cm^{-1} characteristic of C=N stretching vibrations.

Similar changes in the infrared spectra on passing from polyamide–amino-acids to the final polymers were on the whole observed with naphthalenetetracarboxylic and several other dianhydrides [24,31,50,51]. The most characteristic aspect of the transition to the final polymers is the preservation of only one intense band, usually in the range 1695–1720 cm^{-1}, and the absence of the other bands between 1680 and 1800 cm^{-1} which are characteristic of the unfinished polymers. This is consistent with the infrared spectra of corresponding model compounds.

The retention of other bands (at 1775, 1760 cm^{-1}, etc.) on the cyclisation of polyamide–amino-acids based on *oo′*-tetracarboxylic dianhydrides and *oo′*-tetra-amines [41] probably indicates that they are difficult to cyclise in comparison with those based on the corresponding *peri*-compounds.

Pravednikov et al. showed [44] that heating at 150–160°C polyamide–amino-acid films obtained from pyromellitic dianhydride and tetra-amines yields mainly polymers of amino-imide structure. At these temperatures, however, the rate of formation of imide rings is low, and the degree of conversion rapidly reaches a limiting value. Raising the temperature to 200°C did not effect complete cyclisation of the polyamide–amino-acids. This is due to entropy factors (increasing rigidity of the polymer chains) [8,35,52] and also to the possibility that carboxybenzimidazole repeating units may be formed from units in the final structure as a result of hydrolysis by water liberated during cyclisation [8]:

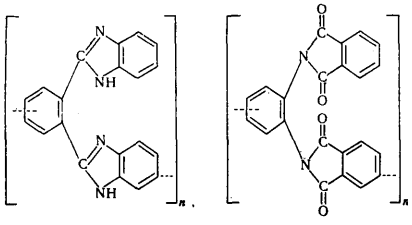


A high degree of conversion of polyamide–amino-acids into the final polymers was achieved at 250–400°C. The

infrared spectra and the elementary composition of polyamide–amino-acid films and powders obtained from naphthalenetetracarboxylic dianhydride and tetra-amines showed, after vacuum heat-treatment, that cyclisation was almost complete at 300–350°C.[31,36,40]

Cross-linking may occur in this temperature range, with the formation of a certain amount of insoluble polymers[31,36]. The intensity of intermolecular cross-linking depends on the mobility of the molecular chains, and is minimal with polymers containing no $-CH_2-$ or $-O-$ hinge groups. A certain quantity (< 5%)of units probably remain uncyclised at these temperatures, and they do not appear in the infrared spectra.

Korshak et al.[34,53] obtained polyimides containing pendant arimide groups attached to the main chain by the interaction of polyamide–amino-acids in solution with anhydrides of aromatic dicarboxylic acids and subsequent heat-treatment. Reaction of polyamide–amino-acids with *o*-phenylenediamine in polyphosphoric acid gave polybenzimidazoles containing benzimide pendants on the main chain of the polymer



(*c*) High-temperature polycondensation in solution

High-temperature polycondensation differs from the low-temperature process in occurring at 115–240°C and yielding polymers predominantly of amino-imide or aroylenebenzimidazole structure. The solvents used were molten phenol, pyridine, dimethylacetamide, dimethyl sulphoxide, 1-methyl-2-oxopyrrolidine, 2,5,8-trioxanonane, and polyphosphoric acid.

Dawans and Marvel[4] heated pyromellitic dianhydride and biphenyl-3,3′,4,4′-tetra-amine in boiling pyridine for 70 h to obtain a 90% yield of a polymer (with $[\eta]_{H_2SO_4}$ = 0.65 dl g^{-1}) corresponding in structure to a polyaminopyromellitimide. Heating the product in a vacuum to 300°C gave a pyrrone. A partly cyclised polymer of higher molecular weight ($[\eta]$ = 0.94 dl g^{-1}) was obtained by heating the reactants in dimethylacetamide at 160°C. Heating the starting materials in a mixture of 2,5,8-trioxanonane and pyridine to 240°C yielded a polymer having a high degree of cyclisation.

Polymeric products, which according to their infrared spectra and elementary composition were similar in structure to a polyaminoimide, were obtained by the reaction of perylenetetracarboxylic dianhydride with biphenyltetra-amine, and also with oxydiphenylenetetra-amine or with diphenylmethanetetra-amine in 1-methyl-2-oxopyrrolidine or dimethyl sulphoxide at 160–200°C, and also in boiling dimethylacetamide[5,7,25,31,37]. They were not soluble in organic solvents, but dissolved in concentrated sulphuric acid and in polyphosphoric acid. The polymers were cyclodehydrated by heating in a vacuum at 350°C.[25,31]

Conducting the single-stage synthesis of pyrrones in polyphosphoric-acid solution enables aromatic tetra-amines that are relatively unstable in air to be replaced by their stable salts, and hence the required proportions of the components to be maintained extremely accurately. Pyrrones with a high degree of cyclisation and the highest molecular weights are obtained in polyphosphoric acid[5,21,24]. Departure from equimolecular proportions of the initial components results in a decrease in the molecular weight of the resulting pyrrones[4,31,36], in contrast to what happens in aprotic solvents.

The temperature of polycondensation in polyphosphoric-acid solution was usually 180–220°C (Table 3). Dawans and Marvel[4] obtained polybenzimidazopyrrolones in this solvent by heating tetra-amine tetrahydrochlorides with pyromellitic dianhydride at 200°C for 2–40 h. The concentration of the reactants was 0.6–3.0 wt.% based on the solvent. The resulting polymers were infusible powders, insoluble in organic solvents but soluble in concentrated sulphuric acid and in polyphosphoric acid. Berlin and his coworkers[5,24,25,31,35–37], as well as Van Deusen et al.[20–21,40], prepared polynaphthoylenebisbenzimidazoles from naphthalenetetracarboxylic dianhydride and tetra-amines. The viscosity (Table 4) and the solubility of the polymers obtained are affected not only by the final temperature of the synthesis but also by the rate of rise in temperature. The optimum temperature is 200–210°C.[31,37] The most rapid rise in viscosity occurs during the first 2 h, after which the rate of rise in viscosity is very small; the reaction can be regarded as almost complete after 6–8 h.

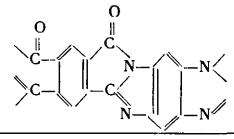
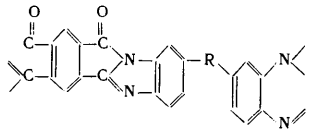
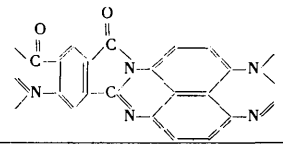
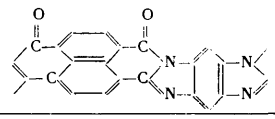
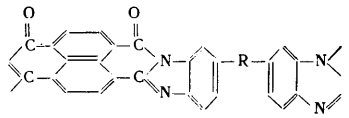
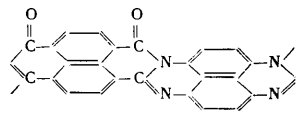
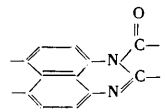
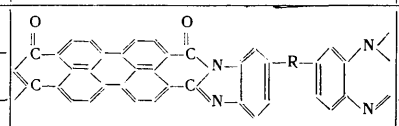
The polymers are soluble in concentrated sulphuric, 85% phosphoric, polyphosphoric, benzenesulphonic, and methanesulphonic acids. They do not decompose on being heated to 320–425°C (the temperature limits of the apparatus)[20,24]. Polymers based on naphthalenetetracarboxylic dianhydride and biphenyltetra-amine dissolve relatively slowly. Solutions of 5–10% concentration have been obtained at ~ 100°C. With polymers based on the same dianhydride and oxydiphenylenetetra-amine or diphenylmethanetetra-amine 5–6% solutions in sulphuric acid can be obtained at room temperature[20]. A method has been worked out for improving the solubility of the polymers by freeze-drying the moist products. This has enabled a porous polymer to be obtained, which is consequently more readily soluble.

Heating pyrrones in a vacuum above the temperature of their synthesis in polyphosphoric acid increases their molecular weight[20,31,37], probably owing to solid-phase polycondensation at the terminal groups. Thus when polynaphthoylenebisbenzimidazole ($[\eta]$ = 0.9 dl g^{-1}) was heated in a vacuum at 215°, 250°, 275°, 300°, and 325°C for 4 h, the intrinsic viscosity of the polymer increased to 1.3 dl g^{-1}; no products insoluble in concentrated sulphuric acid were formed[31,37].

Pyrrones obtained from naphthalenetetracarboxylic dianhydride and a series of tetra-amines possess fibre-forming properties[21,54,55]. X-Ray examination of the polymers shows them to be either amorphous or polycrystalline materials.

Berry and Fox[51] succeeded in reducing a polynaphthoylenebisbenzimidazole (from naphthalenetetracarboxylic dianhydride and biphenyltetra-amine) with dithionite in aqueous pyridine solution. The soluble polymer obtained oxidised readily in the air. The scattering of a laser beam was used to measure the molecular weights of various fractions of the polymer (M = 81 000–167 000 for $[\eta]$ = 2.02–5.48 dl g^{-1}).

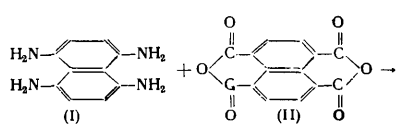
Table 3. Pyrrones obtained by high-temperature polycondensation in solution.

Initial components: dianhydride	Initial components: tetra-amine	Repeating unit	Synthesis conditions: R	Synthesis conditions: temp., °C	Synthesis conditions: solvent	Additional heat-treatment, °C	[Viscosity] in conc. H_2SO_4	Ref.
PMDA	BTA, 4HCl		—	200	PPA	—	1.10	4
PMDA	BPTA, 4HCl		—	160	diglyme or DMAA	—	0.71—0.94[a]	4
PMDA	BPTA		—	200	PPA	—	1.25—1.80[b]	4
PMDA	ODPTA		—O—	200	PPA	—	1.26	4
PMDA	NTA		—	230—300	diglyme	—	0.34—0.41	4
NDA	BTA		—	190—220	PPA	—	0.34—0.90 5	20, 22, 40
NDA	BPTA, 4HCl		—	110—200	PPA	300	0.57—1.90	5, 20, 24, 31
NDA	ODPTA, 4HCl		—O—	200	PPA	300	1.10	31, 35
NDA	DPMTA		$-CH_2-$	200	PPA	300	1.40	31, 35
NDA	NTA		—	180	diglyme	350	0.15[c]	40
Dimethyl 4,5-diaminonaphthalene-1,8-dicarboxylate			—	100—250	PPA	—	0.08—0.25	40
4,5-Diaminonaphthalene-1,8-dicarboxylic anhydride			—	100—250	PPA	—	—	21, 40
PTDA	BPTA, 4HCl		—	230	PPA	350	0.21	25, 31
PTDA	BPTA		—	160—175	DMSO DMAA	350	0.32	25, 31
PTDA	ODPTA		—O—	185—190	MOP	350	0.06	31
PTDA	DPMTA		$-CH_2-$	185—190	MOP	350	0.07	31

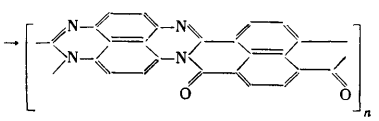
[a]Logarithmic viscosity of 0.25% solution in concentrated sulphuric acid. [b]Intrinsic viscosity measured in DMSO. [c]Logarithmic viscosity in 97% H_2SO_4 at 30°C (0.3 g/100 ml).

The polycondensation of naphthalene-1,4,5,8-tetraamine (I) with naphthalene-1,4,5,8-tetracarboxylic dianhydride (II) and the homopolycondensation of dimethyl 4,5-diaminonaphthalene-1,8-dicarboxylate (III) or the anhydride of the acid (IV) gave polymers (polyperimidinetetrayls) of completely ladder structure[38]:

Scheme 9



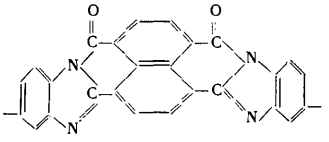
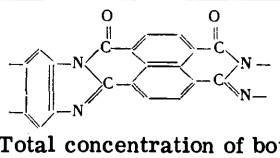
(I) (II)



Since (I) could not be isolated in the free state, it was prepared by catalytic reduction in 2,5,8-trioxanonane, and the dianhydride was added to the resulting solution. The polycondensation was conducted in an atmosphere of nitrogen at 180°C for 12 h; after the trioxanonane had been removed, the polymer was heated in a vacuum at 350°C for 2 h (Table 5). Elementary analysis and infrared

spectroscopy indicated that the polymers were not completely cyclised, which is explained by incomplete reduction of tetranitronaphthalene or oxidation of (I) during polycondensation.

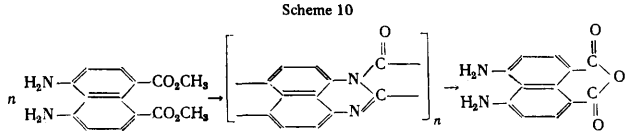
Table 4. Conditions of polycondensation in polyphosphoric acid and viscosity of resulting polymers [20,31].

Repeating unit	Monomer concn., M*	Reaction conditions: temp., °C	Reaction conditions: time, h	Viscosity in conc. H_2SO_4 η
	0.40	110—120	18	0.57
	0.22	180—190	20	1.35
	0.40	200—220	3.5	0.75
	0.12	195—200	8	1.1
	0.12	205—210	8	1.8
	0.20	100—130	18	0.28
	0.18	180—190	20	0.63
	0.13	190—195	24	0.90
	0.19	200—220	4.5	0.34

*Total concentration of both monomers in polyphosphoric acid.

The difficulties associated with the instability of (I) are eliminated by effecting the polycondensation of (III) or (IV) in polyphosphoric acid at 100–250°C:

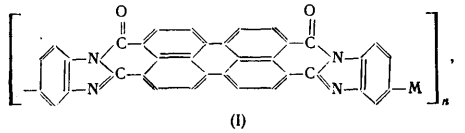
Scheme 10



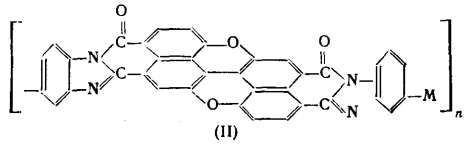
(III) (IV)

Polymers obtained from (III) are soluble in concentrated sulphuric acid. Their elementary composition agrees satisfactorily with calculation. Polymers obtain by the polycondensation of (IV) did not dissolve in concentrated sulphuric acid.

The polycondensation in polyphosphoric acid of the dianhydrides of perylenetetracarboxylic [5,25,31,37] and of 2,8′:2′,8-dioxy-1,1′-binaphthyl-4,4′,5,5′-tetracarboxylic [45] acids with aromatic tetra-amines yields polyaroylene-bisbenzimidazoles having the structures



(I)



(II)

The polymer (V) (M absent, $[\eta] = 0.2–0.3$ dl g^{-1}) was obtained by heating the initial components in polyphosphoric acid to 230°C and maintaining this temperature for 16 h.

When other tetra-amines (M = O, CH_2) were used, the polymers (V) were obtained in low yields and having a smaller value of $[\eta]$. Polymers of structure (VI) (with M absent or representing CH_2) were synthesised at 200 to 210°C. With rise in the temperature and increase in the duration of the synthesis the molecular weight of the polymers (VI) ($[\eta] = 0.6$ dl g^{-1}) increased, but at the same time the yield of insoluble products also increased.

Table 5. Conditions of synthesis and properties of polyperimidinetetrayls [40].

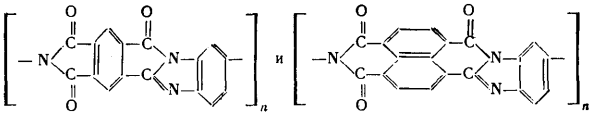
Initial components	Solvent	Temp., °C	Colour of polymer	Logarithmic viscosity**
I + II	diglyme	180 350*	blue	0.15
III	PPA	200	dark blue	0.25
IV	PPA	100	yellow	—
	PPA	200	brown	—

*Temperature of vacuum heat-treatment.
**0.3 g in 100 ml of 97% H_2SO_4 at 30°C.

Pyrrones have been obtained also by using for polycondensation in polyphosphoric acid (at 200°C for 8 h) dianhydrides of bisadducts of diene synthesis between maleic anhydride and various bisfuran compounds [26,37,56].

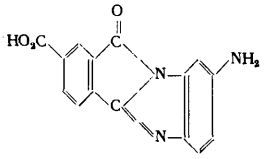
(*d*) Synthesis of polymers akin to pyrrones

D'Alelio and Kieffer [57] obtained high-viscosity polyimidazopyrrolone–imides by the polycondensation of benzene-1,2,4-triamine with the dianhydride pyromellitic and benzophenonetetracarboxylic acids in dimethylacetamide solution followed by thermal cyclisation of the precondensates. The use of naphthalenetetracarboxylic dianhydride gave polymers of very low molecular weight (~ 0.1 dl g^{-1}). The polycondensation of benzene-1,2,4-triamine or its dihydrochloride with pyromellitic or naphthalenetetracarboxylic dianhydride in polyphosphoric acid at 180°C for 12–14 h yielded the polymers



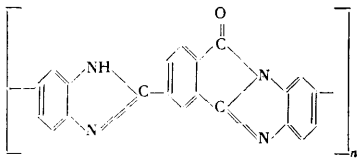
having intrinsic viscosities of 0.63 and 0.88 dl g^{-1} respectively.

The reaction of benzene-1,2,4-triamine with trimellitic anhydride in dimethylacetamide or polyphosphoric acid gave only products of low viscosity, which was attributed to formation of the unreactive compound



Polymers of higher molecular weight ($[\eta] = 0.29–0.45$ dl g^{-1}) have been obtained from trimellitoyl chloride and benzene-1,2,4-triamine in the above solvents in the

presence of triethylamine as acceptor of hydrogen chloride. Polymers ($[\eta] = 0.51$ dl g^{-1}) with the structure



have been obtained by the polycondensation of trimellitic anhydride with biphenyl-3,3′,4,4′-tetra-amine in polyphosphoric acid [57,58].

Copolymers of imidoaroylenebenzimidazole structure were obtained by copolycondensation of the naphthalenetetracarboxylic dianhydride and the biphenyltetra-amine with benzidine or *pp*′-oxydianiline [ODPDA]. [31,59] Various molar proportions of dianhydride, diamine, and tetra-amine (1 : 0.2 : 0.8, 1 : 0.5 : 0.5, 1 : 0.8 : 0.2) were used to synthesise the copolymers. Their synthesis was accomplished either in two stages or as a single-stage process in polyphosphoric acid. The first stage in the two-stage synthesis involved heating the mixture of dianhydride, diamine, and tetra-amine in dimethylacetamide, dimethyl sulphoxide, or 1-methyl-2-oxopyrrolidine at 75–85°C for 6 h. Subsequent vacuum heat-treatment of the precondensates at 200–300°C effects their intramolecular cyclisation to form copolymers of block-ladder imidoaroylenebenzimidazole structure. In the single-stage method polycondensation was conducted in polyphosphoric acid at 200°C for 8 h. Owing to the difference in activity between diamines and tetra-amines the composition of the copolymers differed from that of the initial mixture. The final copolymers were dark, amorphous powders, soluble in polyphosphoric, sulphuric, and formic acids but insoluble in organic solvents. Their intrinsic viscosity was 0.2–0.6 dl g^{-1}.

IV. PROPERTIES OF THE POLYMERS

1. Thermal Stability

The main property which first attracts the attention of research workers to pyrrones is their high heat-resistance and thermal stability. Despite the heightened interest in such polymers, only isolated papers have hitherto been specially concerned with a detailed investigation of their thermal stability. In most publications, however, the thermal stability of the pyrrones obtained is measured by thermogravimetric curves determined with different rates of temperature rise. This makes it difficult to compare the thermal stability of pyrrones differing in structure. Furthermore, very little information is given on the chemistry of the processes occurring in the polymers at high temperatures in oxidising and inert atmospheres and also in a vacuum.

Several workers [60–63], who have investigated the mechanism of the degradation of polymers containing heterocycles in the main chain (polyimides, polybenzimidazoles, polyoxadiazoles, etc.), associate the thermal stability of the polymers mainly with the stability of the heterocycles. This takes no account of the specific natures of the polymers examined, which are governed by the presence of a system of conjugated bonds extending through large sections of the macromolecular chain and by the presence of paramagnetic centres whose structure does not remain constant over a wide temperature range [64,65,67].

Dawans and Marvel [4] used a dynamic thermogravimetric method to study thermal degradation, and showed that polybenzimidazopyrrolones based on pyromellitic dianhydride are stable in an atmosphere of nitrogen up to 450 to 500°C; at 800–900°C they undergo a loss in weight of 25–40%. In air these polymers are oxidised fairly rapidly at 350–400°C. The thermal stability of pyrrones prepared in polyphosphoric acid is superior to that of the same polymers obtained in two stages and in the melt (Fig. 1)‡. The presence of intermediate methylene or oxygen links in the macromolecular chain leads to some diminution in the thermal stability of the polymers (Figs. 2 and 3). Polybenzimidazopyrrolones based on benzophenonetetracarboxylic acid show thermal stability as good as that of the corresponding polymers based on pyromellitic dianhydride (Fig. 3).

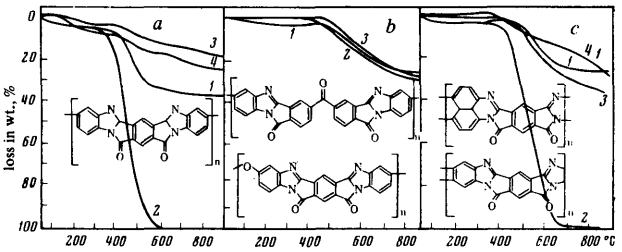
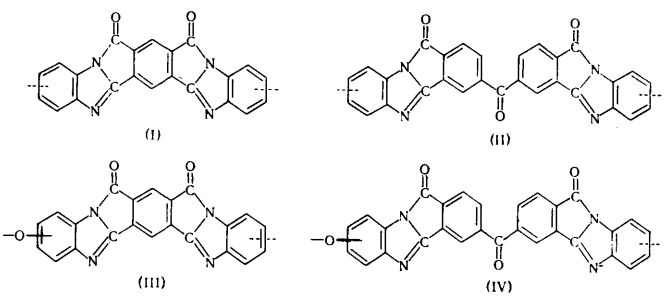


Figure 1. Thermogravimetric curves (rate of rise in temperature $\Delta T = 6$ deg min^{-1}) obtained in air for polymers prepared in: *a*) 1) melt; 2) melt (curve in nitrogen); 3) PPA soln.; 4) two stages; *b*) 1) melt; 2) melt; 3) PPA soln.; *c*) 1) melt; 2) melt (curve in nitrogen); 3) melt; 4) PPA soln.

In a study of the thermal degradation under isothermal conditions of films of the pyrrones



Jewell found [66] that the initial losses in weight were due to removal of absorbed moisture (~ 7 wt. % up to 100–150°C) and to further intramolecular cyclisation. Films which had been preheated at 350°C for 2 h did not lose weight until progressive decomposition of the polymer occurred, which began above 400°C (Fig. 4).

‡Pyrrones obtained in the melt under high pressure possess enhanced thermal stability in air and in an inert atmosphere [47].

The effective activation energy of thermo-oxidative degradation, calculated for the polymers (I)–(IV) from the constant-rate sections over the range 440–460°C, was respectively 31, 34, 28, and 30 kcal mole^{-1}. The authors concluded from the results of differential thermal analysis that the polymers had undergone no phase transitions.

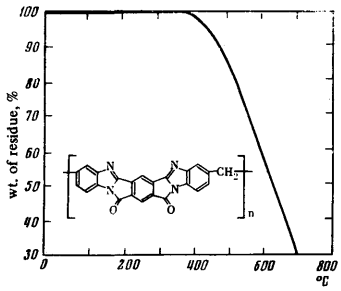


Figure 2. Thermogravimetric curve (ΔT = 4 deg min^{-1}) in air.

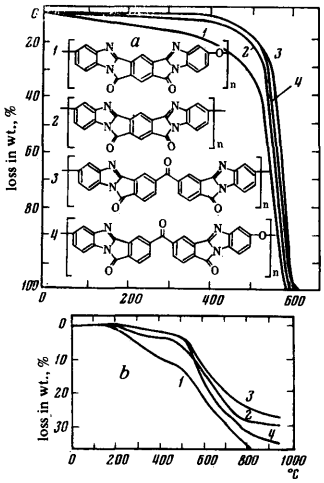


Figure 3. Thermogravimetric curves for pyrrone films (ΔT = 5 deg min^{-1}) in: *a*) air; *b*) vacuum.

When the polymers are heated in a vacuum, the main losses in weight are observed during the initial period of degradation, after which the weight of the residue tends to a limiting value. The total losses in weight of the pyrrones investigated are 28–38 wt. % up to 800°C. The activation energy for degradation of the polymers (I)–(IV) in a vacuum is 47–50 kcal mole^{-1}.

Examination of the products of the degradation of polymer (II) showed that up to 380°C the losses in weight are due to the removal of water. Above 420°C a successive increase in the rate of degradation is observed; it reaches a maximum at 550°C, and drops rapidly at temperatures above 620°C. A large quantity of carbon monoxide and dioxide is evolved in this temperature range. At about 500°C –NCN–groups are also eliminated. With rise in temperature to 650°C these are accompanied by CN– and HCN– groups. Evolution of traces of ammonia is observed only during the main decomposition of the polymer. Thus dehydration occurs in the initial period, and this is followed by thermal rupture of bonds in the macromolecular chain.

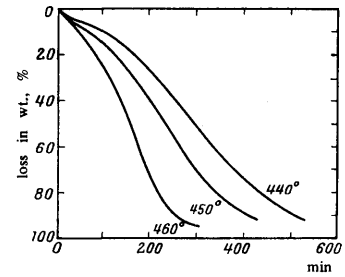


Figure 4. Thermogravimetric curves for pyrrone film (BODA–BPTA) in air.

An investigation of thermo-oxidative degradation undertaken by the Reviewers [5,24,31,35,67] and also by Van Deusen and his coworkers [6,20,40] indicates that polynaphthoylene-bisbenzimidazoles are more stable than the corresponding polyimides and also than pyrrones based on pyromellitic dianhydride (Fig. 5) Their resistance to thermo-oxidative degradation is found to depend, up to a certain limit, on the molecular weight, which is probably an effect of the terminal groups. A particularly substantial decrease in stability was observed with polymers of low molecular weight: when $[\eta]$ = 0.37 dl g^{-1}, progressive breakdown began at a temperature 75 deg lower.

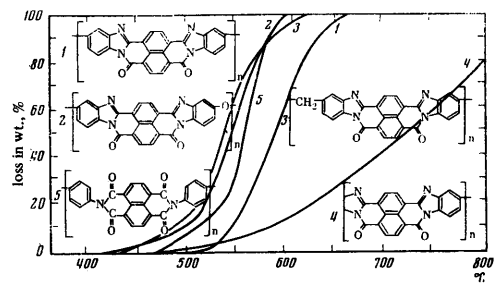


Figure 5. Thermogravimetric curves in air with ΔT = 2 deg min^{-1} (2.5 deg min^{-1} for curve 4).

In a vacuum or in an inert atmosphere the polymers lose 18–30% in weight when heated to 800–900°C. The influence of molecular weight is considerably less evident under these conditions, but even in this case polymers having low molecular weights begin to lose weight at lower temperatures. Polymers obtained from naphthalene-tetracarboxylic dianhydride and biphenyltetra-amine, having intrinsic viscosities of 0.8–1.15 dl g^{-1}, do not

decompose at all when heated in nitrogen to 600°C (Fig. 6), whereas a similar polymer of viscosity 0.12 dl g^{-1} loses up to 10 wt.%. Polymers of completely ladder structure obtained from naphthalenetetracarboxylic dianhydride and benzenetetra-amine, lose 4 wt.% under the same conditions. Several authors [52] explain the lower thermal stability of polymers of ladder structure, probably correctly, by the absence of extensive polyheterocyclisation on rigid macromolecules, i.e. by the presence of a large number of defects.

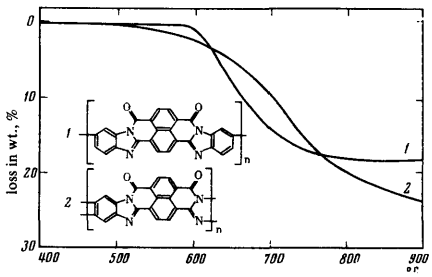


Figure 6. Thermogravimetric curves in nitrogen (ΔT = 2.5 deg min^{-1}).

Differential thermal analysis of a polynaphthoylenebisbenzimidazole (from naphthalenetetracarboxylic dianhydride and biphenyltetra-amine) (Fig. 7) has shown [31] that reactions involving complicated intra- and intermolecular rearrangements occur when the polymer is heated in an inert atmosphere, in an inert atmosphere contaminated with air, and in air. Heating the polymer to 110–120°C reveals an endothermic peak, indicating the evolution of 4–5% of adsorbed water. Raising the temperature to 270–330°C leads to cyclisation of the repeating units that have remained uncyclised, accompanied by the appearance of an exothermic peak on the curves. Further heating of the polymer in air to 540°C and in argon to 655°C produces insignificant losses in weight, but above these temperatures the specimen breaks down rapidly in air, and loses up to 20–25 wt.% in an inert atmosphere. Breakdown of the polymer is accompanied by cross-linking. The most favourable conditions for carbonisation occur in an inert atmosphere. In air and even with a low oxygen content (7%) degradative processes predominate over cross-linking processes, resulting in progressive weight losses by the polymer.

Tests on the isothermal aging of pyrrones (from naphthalenetetracarboxylic dianhydride and biphenyltetra-amine) showed that they lost only 10 wt.% after being heated in air at 315°C for 1500 h. [20] At 400°C the weight losses for a polymer of the same type do not exceed 10% after 7–8 h.

A kinetic study of the thermo-oxidative degradation of this polymer has been made over the range 450–570°C (Fig. 8). [31,67] The process is clearly autocatalytic in character. The effective activation energy, calculated for sections having a constant rate, is 28.8 kcal $mole^{-1}$ in the temperature range 470–502°C. At higher temperatures the process takes place without an induction period, and its activation energy falls to 7.4 kcal $mole^{-1}$, which indicates a change in the mechanism of thermo-oxidative degradation,

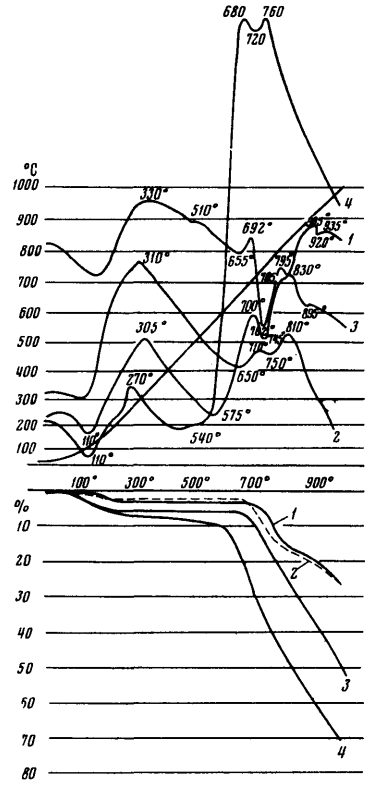


Figure 7. Differential thermal analysis of polynaphthoylenebisbenzimidazole (NDA–BPTA) with ΔT = 6 deg min^{-1} in: 1) argon (under cover); 2) argon (open crucible); 3) argon + 7% O_2; 4) air.

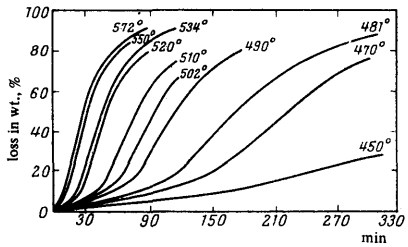


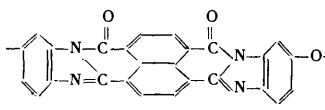
Figure 8. Thermogravimetric curves in air for polynaphthoylenebisbenzimidazole (NDA–BPTA, $[\eta]$ = 1.0 dl g^{-1}).

Small (1%) additions of the previously pyrolysed polymer produce an increase in the maximum rate of degradation. The autocatalytic character of degradation of the polymer and the specific effect of pyrolysed additions are explained in terms of a "local activation effect", which is characteristic of polymers containing a conjugated system [65,67].

Mass-spectroscopic analysis indicates that, when polynaphthoylenebisbenzimidazoles are heated in a vacuum to 800°C, the chief gaseous products are carbon monoxide, nitrogen, and a certain amount of carbon dioxide; hydrogen and steam are also evolved. These results, together with

the composition of the residues (Table 6), indicate the occurrence of processes of carbonisation and the formation of polynuclear fused systems, including conjugated carbocyclic and heterocyclic rings.

Table 6. Change in composition of polymer after being heated in a vacuum [31,37,50].

Repeating unit	Composition	Temperature at which heated, °C				
		300	400	500	600	800
	C/N	5.6	5.8	5.7	9.7	10.9
	C/H	27.7	29.5	30.7	47.5	61.3

Thermogravimetric analysis of the thermal and thermo-oxidative degradation of pyrrones obtained from perylene-tetracarboxylic dianhydride with biphenyltetra-amine, oxydiphenylenetetra-amine, and diphenylmethanetetra-amine respectively (Fig. 9) [24,31,67] indicates that these polymers are less stable in air than are the corresponding polynaphthoylenebisbenzimidazoles of high molecular weight ($[\eta] \geq 1.0$ dl g^{-1}). Nevertheless, they are more resistant to thermo-oxidative degradation than are polynaphthoylenebisbenzimidazoles of low molecular weight ($[\eta] < 0.4$ dl g^{-1}). Such a difference is probably due to the influence of the terminal groups. In a vacuum their thermal stability is equal to or even somewhat surpasses that of polynaphthoylenebisbenzimidazoles of high molecular weight, which is probably due to the stronger intermolecular interaction of polymers containing perylene rings and their greater tendency to cross-linking.

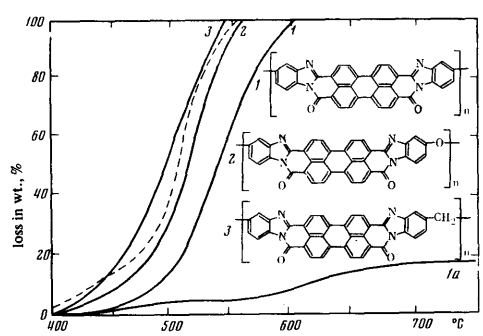
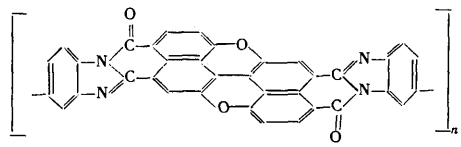


Figure 9. Thermogravimetric curves (ΔT = 2 deg min^{-1}) in: 1)–3) air; 1*a*) vacuum; ---) polynaphthoylenebisbenzimidazole (NDA–BPTA, $[\eta] = 0.37$ dl g^{-1}).

Great thermal stability in air and in a vacuum is shown also by pyrrones prepared in polyphosphoric acid from biphenyltetra-amine and dianhydride bisadducts of maleic anhydride with bisfuran compounds [26,56], and also from this tetra-amine and 2,8′ : 2′,8-dioxy-1,1′-binaphthyl-4,4′,5,5′-tetracarboxylic dianhydride.[45]



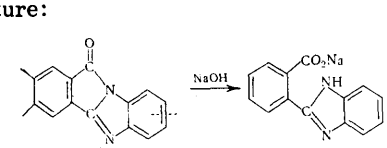
As has been mentioned above, the application of thermostable polymers is most promising in space technology. Such polymers and also compositions based on them are used for the ablation protection of the surfaces of aircraft and propulsion units from the action of high-temperature gas-flows. Prospects have been discussed [68] for the use of heterocyclic polymers of ladder and block–ladder structure as ablation-resistant coatings. Many pyrrones prepared from aromatic tetra-amines and various dianhydrides (of naphthalenetetracarboxylic acid, perylene-tetracarboxylic acid, bisadducts of diene synthesis between maleic anhydride and bisfuran compounds) proved resistant to the action of high-temperature air flows [69–72]. They satisfy such criteria of ablation resistance as low rate of ablation $A_V = \Delta m/\tau F$ kg m^{-2} s^{-1} (where Δm is the loss in weight, F the surface area of the specimen, and τ the duration of the test) and resistance to the action of large temperature gradients. Specimens of the polymers and compositions were prepared by hot pressing.

The rate of ablation of a polymer is almost independent of its molecular weight after the latter has reached a certain value ($[\eta] \geq 0.9$ dl g^{-1}), being determined by its resistance to thermo-oxidative degradation and its tendency to cross-linking. Pyrrones based on naphthalenetetracarboxylic dianhydride, and especially those containing perylene rings, showed the lowest rate of ablation. The introduction of intermediate oxy and methylene groups somewhat increases the rate of ablation. Polymers having a low degree of cyclisation exhibited a sharp drop in ablation resistance. Pyrrones show better ablation resistance than corresponding polyimides and unmodified phenol–formaldehyde resins. The stability of the test specimens to the action of a temperature gradient is greatly improved after they have been heat-treated in an inert atmosphere; it is improved also by hot-pressing polymers containing additives which act as temporary plasticisers.

2. Resistance to Radiation and Chemicals

Pyrrones are extremely resistant to the action of ionising radiation (Table 7). Thus the strength properties of pyrrone films had not deteriorated after exposure to a 10 000-Mrad dose of electrons of energy 2–3 MeV, whereas polyester films are destroyed by a dose of 200 Mrad. [3,19,73,74]

Investigation of the chemical stability of polybenzimidazopyrrolones has shown that the mechanical strength of the films diminishes relatively slowly on standing in 96% sulphuric acid (Table 8). In alkaline solutions the films rapidly lose their strength. The reaction between the polymer and the alkali can be regarded as conversion of the imidazopyrrolone structure into a polycarboxybenzimidazole structure:



Polynaphthoylenebisbenzimidazoles, in contrast to polybenzimidazopyrrolones, are extremely resistant to the action of concentrated sulphuric acid[31,36]. The viscosity of solutions of the polymers is almost unchanged after standing in the acid at room temperature for 700 h. Keeping a polynaphthoylenebisbenzimidazole in 40% alkali (potassium hydroxide) for 2 days produces a decrease in its intrinsic viscosity from 1.8 to 1.1 dl g^{-1}.

Table 7. Effect of radiation on mechanical properties of pyrrone films[3,19].

Pyrrone film	Dose, Mrad	Stress at flow point, kg cm^{-2}	Tensile strength, kg cm^{-2}	Relative elongation, %	Young's modulus, kg cm^{-2}
PMDA-BPTA*	0	930	1 170	3.2	56 800
	1 100	995	1 460	4.5	61 800
	5 500	1 010	1 460	3.9	62 200
	11 000	1 020	1 340	3.1	62 400
	21 000	1 090	1 560	3.3	69 200
	58 300	875	1 070	2.7	57 800
PMDA-ODPTA**	0	647.9	1 260	9.0	51 408
	1 000	859.1	1 183	3.0	58 450
	5 000	1 007	1 422	3.0	57 756
	10 000	1 098	1 218	3.0	60 000

*Temperature of cyclisation 300°C; temperature of exposure 250°C; beam of electrons of energy 3 MeV; dosage rate 5500 Mrad h^{-1}.
**Irradiated with electrons of energy 2 MeV; dosage rate 1000 Mrad h^{-1}.

Table 8. Chemical stability* of polybenzimidazopyrrolone film[19].

Reagent	Young's modulus, kg cm^{-2}	Relative elongation, %	Tensile strength, kg cm^{-2}
Initial film	43 000	5.5	1 560
	27 500	7.5	900
96% H_2SO_4	41 600	4.6	1 190

*Films 0.025 mm thick cyclised at 250°C (for 1 h). Specimen kept at room temperature (for 1 h), washed with water, and dried at room temperature for 1 h.

3. Electrical, Magnetic, and Catalytic Properties

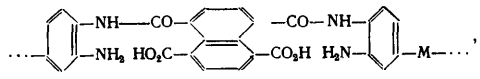
Very little information is available on the electrical properties of polybenzimidazopyrrolones[3,4]. Their resistivity and dielectric strength are typical of insulating organic polymers (Table 9). Polybenzimidazopyrrolones are paramagnetic materials having concentrations of unpaired electrons of 10^{16}–10^{19} g^{-1}.[7]

The magnetic and electrical properties of polymers based on naphthalenetetracarboxylic and perylenetetracarboxylic dianhydrides with aromatic tetra-amines, and also of copolymers of naphthalenetetracarboxylic dianhydride with diamines and tetra-amines, have been studied in greater detail[5,24,25,31,35,50]. The temperature dependence of the conductivity of these polymers is typical of organic semiconductors. Table 10 shows that the conductivity parameters (the activation energy E_σ and the resistance ρ_t) depend substantially on the nature of the dianhydride and the tetra-amine used and on the ratio of diamine and tetra-amine in the case of the copolymers. A break in the conjugated system impairs the conductivity. With increase in the number of fused rings in the initial dianhydride the values of ρ and E_σ for the polymers diminish, probably owing to an increase in intermolecular interaction.

Table 9. Electrical properties of polymers[3,4].

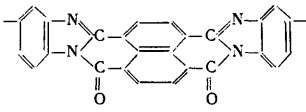
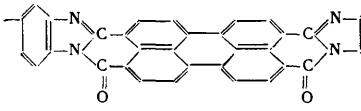
Polymer		Resistivity, ohm cm	Dielectric strength, V cm^{-1}	Dielectric constant
PMDA-ODPTA	PAAA	$6 \cdot 10^9$	$2 \cdot 10^5$	—
	pyrrone	$(3—5) \cdot 10^{12}$	$6 \cdot 10^5$	—
PMDA-NTA	pyrrone	$5 \cdot 10^{10}$	—	4.0

Polyamide-amino-acids have lower conductivities, which depend to a less extent on the nature of M in the formula[31,50]



(where M represents O or CH_2 or is absent).

Table 10. Electrical properties of polyaroylenebisbenzimidazoles and copolymers[31,50].

Polymer		No.	—M—	Conductivity measured up to 200°C: E_σ	Conductivity measured up to 200°C: $\lg \rho_{150°}$
		I	absent	0.47	5.70
		II	—O—	0.67	9.35
		III	$—CH_2—$	0.57	8.35
		IV	absent	0.32	4.60
		V	—O—	0.48	7.10
		VI	$—CH_2—$	0.42	6.50
NDA-BPTA-ODPDA copolymers	1:0.2:0.8	VII	—	0.74	9.75
	1:0.5:0.5	VIII	—O—	0.60	7.60
	1:0.8:02	IX	—	0.59	6.25

Both the final polymers and the precondensates give electron spin resonance signals characteristic of conjugated polymers[5,24,25,31,35,50]. The concentration of paramagnetic centres is considerably lower in polyamide-amino-acids than in cyclised polymers. The paramagnetism of the former compounds has been explained[24] by the possibility of formation of an isoimide structure. In such polymers, moreover, intramolecular and intermolecular transmission of conjugation can be accomplished by complex formation between amino- and carboxy-groups.

A study has been made of the variation in the electrical properties at various stages in the production of polymer molecules when polyamide–amino-acids are heated in a vacuum from 50–100° to 800°C.[31,37,50] The various polyamide–amino-acids show a general tendency for the electrical and magnetic properties to change with the temperature at which they have been heated (Fig. 10). Only intramolecular cyclisation occurs up to 150–200°C. Above 300°C this is accompanied by incipient slight cross-linking (depending on the structure of the polyamide–amino-acid and the polymer), which intensifies at 400°C. In this temperature range the electrical properties of the polymer improve, the narrow e.s.r. signal becomes stronger and narrower, the background in the infrared spectra becomes stronger, and amorphous specimens become polycrystalline.

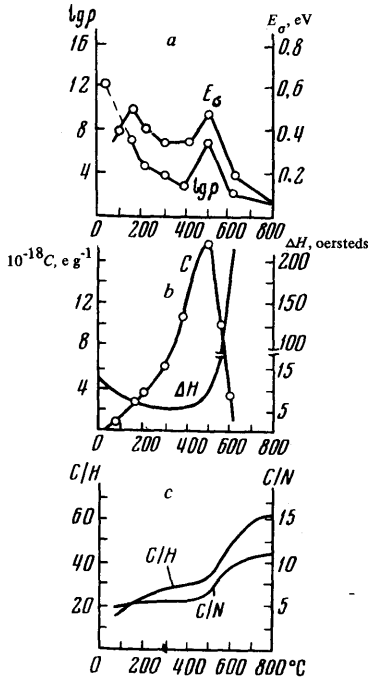


Figure 10. Change in electrical properties—E_σ and ρ_t—and magnetic properties—C (e g^{-1}) and ΔH_{esr} (oersteds)—and in elementary composition of PAAA on heating in a vacuum (for 2 h at each temperature).

Processes involving partial degradation of macromolecules at weak bonds (structural defects) begin at 500°C. They are accompanied by a diminution in the degree of order in the polymer specimen and a sharp deterioration in electrical properties. At 600°C the evolution of gaseous products is accompanied by that of heavier, reactive fragments able to sublime, recombination occurs, blocks previously formed on degradation undergo further cross-linking, the electrical properties of the polymers improve, the intensity of the narrow e.s.r. signal decreases, and a broad e.s.r. signal appears. Raising the temperature of pyrolysis to 800°C leads to a further improvement in the electrical properties and very considerable broadening of the e.s.r. signal of the residues, which contain a notable quantity (up to 8%) of nitrogen and a certain amount of oxygen, and are probably coarse blocks of a polycyclic aromatic including heterocyclic rings.

Pyrrones are catalysts of semiconductor type[7,75,76]. The decomposition of nitrous oxide was found to depend in considerable measure on the type of conjugation in the catalyst macromolecules. Thus the activation energy for this model reaction was 40–52 and 18–27 kcal mole^{-1} when pyrrones of block–ladder and ladder structure respectively were used.

Table 11. Mechanical properties of pyrrone films[19].

Pyrrone	Tensile strength, kg cm^{-2}	Elongation, %	Young's modulus, kg cm^{-2}
PMDA-BPTA	1430	2.8	66 500
PMDA-ODPTA	1530	4.8	57 000
PMDA-DPMTA	975	3.9	37 400
PMDA-BOTA	930	2.6	41 500
BODA-BPTA	1420	4.3	42 000
BODA-ODPTA	1320	3.8	43 800
BODA-DPMTA	680	1.9	41 900
BODA-BOTA	840	3.1	34 800

4. Mechanical Properties

In view of the great thermal stability of pyrrones they show promise for the production of films, adhesives, fibres, and moulded articles. The strength of pyrrone films is high[19], but, as was to be expected with such rigid chains, they have a high modulus of elasticity and low relative elongation (Table 11). The mechanical properties of the films is greatly influenced by the temperature of cyclisation (Table 12) and to a less extent by the atmosphere in which cyclisation occurs (Table 13). The effect of the test temperature on the strength properties of pyrrone films is shown in Table 14.

Table 12. Effect of temperature of cyclisation on mechanical properties of PMDA–BPTA pyrrone films (duration of cyclisation 1 h).[19]

Temp. of cyclisation, °C	Tensile strength, kg cm^{-2}	Stress at flow point, kg cm^{-2}	Young's modulus, kg cm^{-2}	Elongation, %
150	775	1 140	35 600	5.4
225	920	1 200	38 200	4.1
300	1 030	1 320	44 000	3.8

Pyrrone films are far stronger than those obtained from polyamide–amino-acids. For example, the tensile strength of the latter films based on pyromellitic dianhydride and oxydiphenylenetetra-amine is 704–1060 kg cm^{-2}, whereas that of the corresponding pyrrone film[3] is 1060–1550 kg cm^{-2}. Strong films have been obtained from

polyamide-amino-acids prepared from naphthalenetetracarboxylic dianhydride with oxydiphenylenetetra-amine and with diphenylmethanetetra-amine [31,36], their tear strengths being respectively 910 and 850 kg cm^{-2}. After cyclisation at 300°C the strength of the films had improved to 1200 and 1040 kg cm^{-2}. Their mechanical constants can probably be improved by finding optimum conditions for production of the films.

Table 13. Effect of atmosphere on mechanical properties of PMDA–BPTA films (heated at 250°C for 3 h). [19]

Atmosphere	Tensile strength, kg cm^{-2}	Elongation, %	Young's modulus, kg cm^{-2}
Air	1090	4	48 600
Vacuum	1100	3.8	47 600
Nitrogen	990	2.1	60 000

Table 14. Effect of temperature of testing on mechanical properties of PMDA–BPTA films [19].

Temp., °C	Stress at flow point, kg cm^{-2}	Tensile strength, kg cm^{-2}	Elongation, %	Young's modulus, kg cm^{-2}
25	900	1190	2.8	60 000
100	685	1110	3.7	50 000
200	529	800	3.7	36 800

Fibres have been obtained from polymers based on naphthalenetetracarboxylic dianhydride and biphenyltetra-amine [21,54,55,77]. Concentrated sulphuric acid was used as solvent in wet spinning. Polymers having intrinsic viscosity 1.15–2.45 dl g^{-1} have been employed. After drawing (at 360–540°C) the strength of the filaments was 0.85–1.33 g $denier^{-1}$ at draw ratios of 1.10–1.29; the elongation at rupture was 6.8–10.0%. With continuous drawing of filaments at 260–565°C and draw ratios of 1.06–1.31 in an atmosphere of argon and in air their strength reached 2 g $denier^{-1}$ at an elongation of 19%. To obtain strong filaments while preserving high values of the elongation at break, a monofil was subjected to hot drawing in argon. Filaments of strength 4 g $denier^{-1}$ were obtained with 4–5% elongation at break. With a filament which had been drawn at 650°C this elongation had decreased to 3%. According to these workers' results wet spinning from solutions in concentrated sulphuric acid can be used for the practical production of a thermostable fibre. The resulting fibre retains 55% of its initial strength after being kept in air at 600°C for 1 min, and 50% in air at 360°C for 30 h; it is extremely resistant to ultraviolet radiation.

Intensive research is being conducted in the USA into the synthesis of high molecular-weight pyrrones of ladder structure (naphthalenetetracarboxylic dianhydride–biphenyltetra-amine) and the production of fibres from them [21,22].

Methods have recently been found for moulding strong, thermostable articles from pyrrones by adding a temporary plasticiser [31,72]. Polymeric goods obtained directly from the molten monomers under high pressures also possess great strength and hardness [47].

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Fluorine-containing Polyethers, polyesters, and polythia-compounds

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Methods of preparation and the influence of fluorine atoms on the principal physicochemical characteristics of fluorine-containing polyethers, polyesters, and polythia-compounds are reviewed. Heterochain and carbochain polyethers and polyesters and their possible regions of practical use in chemistry and technology are discussed. 197 references.

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I. INTRODUCTION

The development of atomic energy, chemical technology, radio electronics, high-altitude aviation and space-flight, and other important branches of technology requires the creation of new polymeric materials which can be used under extremely severe conditions. Here the material should not only withstand contact with various aggressive media but also retain a complex of physicochemical and strength characteristics in these media over a wide range of high and low temperatures. One of the promising directions for increasing the thermal and chemical stability of polymeric materials is the replacement of the hydrogen atoms in them by fluorine atoms. Here the maximal effect can be reached when completely fluorinated monomers are used for the preparation. However, in several instances a considerable improvement in physicochemical properties of the polymeric materials can be brought about by the introduction into their chain of individual fluorine atoms or small perfluorinated groups. Polymers in which the fluorine atoms are linked to carbon are of the greatest practical interest. Systems in which fluorine is bound to silicon, phosphorus, nitrogen, etc. usually are not very resistant to hydrolysis and are not of practical interest for the preparation of high-molecular-weight compounds.

Non-fluorinated polyethers, polyesters and polythia-compounds can be readily converted into rubbers, films, fibres, etc. However, their thermal and chemical stabilities are low, which restricts the range of practical use of these comparatively accessible and cheap materials. The preparation and study of the properties of fluorine-containing polyethers and polyesters have been dealt with in a large number of papers. Both completely fluorinated polyethers and polyesters and also polymers having chains containing various lengths of non-fluorinated substituted methylene groups are of interest.

The present review deals with methods of obtaining fluorine-containing polyethers, polyesters, and polythia-compounds which contain oxygen or sulphur atoms in the main or side polymeric chains. The contribution of the fluorine atoms to the change in physicochemical properties of these polymers in comparison with their non-fluorinated analogues is discussed. Without any pretence of a complete survey of the published material, the review nevertheless reflects sufficiently adequately the general state of the problem of fluorine-containing polyethers, polyesters, and polythia-compounds and makes orientation in this important part of polymer chemistry somewhat easier.

II. POLYETHERS

The $-CF_2-O-CH_2-$ grouping of low stability chemically[1,2] and therefore its introduction into polyether chains is undesirable. Completely fluorinated ethers of the $-CF_2-O-CF_2-$ type exhibit high thermal and chemical stability. The energy of the C–O–C bond in non-fluorinated ethers is ~90 kcal mole^{-1}, whereas for fluorinated ethers it is ~10 kcal mole^{-1} greater. If it is assumed that the energy of the C–C bond in polytetrafluoroethylene is also 90 kcal mole^{-1}, then evidently the introduction of oxygen atoms into a chain consisting of difluoromethylene groups does not reduce the thermal stability of the polymer, but confers upon it several new properties. Methods for the preparation of fluorine-containing polyethers and polythia-compounds are given below and some of their physicochemical properties are described.

A. Heterochain Polyethers and Polythia-compounds

1. Reaction of fluorine-containing alkenes with oxygen. At the beginning of this century, Swarts showed[3] that acyl halides are formed in the oxidation of fluorinated alkenes by oxygen. Subsequently[4,5] further investigation of this process disclosed a tendency of perfluoroalkene–oxygen systems to explode. In the oxidation of tetrafluoroethylene with molecular oxygen at atmospheric pressure[6] using ultraviolet radiation or X-rays as initiator or under the influence of elevated temperature, in addition to simple oxidation products (COF_2, CF_2-CF_2 (O), CF_2-CF_2 (CF_2), etc.) a polymer of composition $(-CF_2CF_2-O-O-)_X$ is formed. The latter is an unstable copolymer of tetrafluoroethylene and oxygen. It was suggested that the oxidation of tetrafluoroethylene proceeds by a chain mechanism[7]. In the absence of

initiators liquid tetrafluoroethylene copolymerises with oxygen at elevated pressure, forming an elastic product with 0.76 mole oxygen per mole tetrafluoroethylene[8]. In the presence of ozone the induction period of the reaction between oxygen and tetrafluoroethylene is shortened but the ozone does not affect the composition of the copolymer[9,10]. A study of the ^{19}F NMR spectra showed that the copolymer has a homogeneous structure $(-CF_2CF_2-O-O)_X$. Evidently, the oxidation of halogenated alkenes takes place analogously to copolymerisation[11], when one of the monomers is incapable of homopolymerisation. A study of the kinetics of oxidation of tetrafluoroethylene by molecular oxygen[12], under the influence of γ- or X-rays confirmed the suggestion of the formation of intermediate products of peroxide type. The reaction of tetrafluoroethylene with oxygen is an autoxidation of the alkene, which is accelerated in the presence of traces of ozone, and is evidently linked with the radical copolymerisation of alkenes with oxygen. Chain growth can be represented by the scheme[10]:

$$\ldots -CF_2^{\cdot} + O_2 \rightarrow \ldots CF_2-O-O^{\cdot} + CF_2=CF_2 \rightarrow \ldots CF_2-O-O-CF_2CF_2^{\cdot}$$

The formation of gaseous products—carbonyl fluoride and tetrafluoroethylene oxide—takes place in the decomposition of the copolymer:

$$\ldots -CF_2-O-O-CF_2CF_2-O^{\cdot} - \ldots -CF_2-O-O-CF_2^{\cdot} + COF_2$$

$$\ldots -CF_2-O-O-CF_2CF_2^{\cdot} - \ldots -CF_2-O^{\cdot} + CF\underset{O}{\diagdown\!\diagup}CF_2.$$

The formation of a peroxide polymer with molecular weight up to 1000 as one of the main reaction products was also noted in the oxidation of chlorotrifluoroethylene[13]. The side-products isolated in this process[14] were COF_2, COFCl, $CF_2Cl-COCl$, and evidently

$$CF_2\underset{O}{\diagdown\!\diagup}CFCl \text{ and } \begin{matrix} CF_2-CFCl \\ | \quad | \\ O-\!-O \end{matrix}[14].$$

When peroxide polymers are heated in an atmosphere of nitrogen the polymer $[-CF_2CF_2-O-]_X$ is formed, in addition to the gaseous products[8]; it exhibits high thermal and chemical stability. Poly(tetrafluorooxyethylene) is a crystalline and rather well orientated polymer with a spiral conformation of the macrochains[15].

Polyethers with a large number of successively linked difluoromethylene groups can be obtained in the common pyrolysis of the mercury salts of perfluorodicarboxylic acids[16]:

$$HgOOC-[CF_2]_n-O-[CF_2]_n-O-[CF_2]_n-COOHg + HgOOC-[CF_2]_y-COOHg \rightarrow \rightarrow [-O-[CF_2]_m-]_x$$

In the pyrolysis of this polymer up to 400°C there is partial cross-linking of its chain occurs. By heating iodides in the presence of mercury[17]:

$$O(CF_2CF_2\dot{I})_2 \xrightarrow[UV]{Hg} -[CF_2CF_2-O-CF_2CF_2-]_x$$

polyethers with $\bar{M}_n \simeq 40\,000$ were obtained. Their glass point is $\sim -65°C$, they withstand solvents and exhibit high thermal stability. Appreciable decomposition of these polyethers is observed above 500°C, which not only exceeds the decomposition temperature of non-fluorinated polyethers but even that of such a thermally stable polymer as poly(tetrafluoroethylene). As a result of the investigation of the thermal degradation of poly(tetrafluoroethylene oxide)[18] it was found that its maximal rate of decomposition is observed at 628°C, with the activation energy of the decomposition being 98 kcal mole^{-1}, whereas for poly(tetrafluoroethylene) these values are 568°C and 85 kcal mole^{-1} respectively. Evidently, the higher thermal stability of poly(tetrafluoroethylene oxide) is due to the greater stability of the radicals formed in the degradation.

The polyesters based on perfluoropropene are of considerable interest and have already found practical application. The nature of the initiator employed has a considerable influence on the course of the reaction between oxygen and perfluoroethylene. With γ-rays, gaseous products are mainly formed[19], the bulk of which consists of COF_2 and CF_3-COF, and there is a small quantity of an explosive polymer with M = 120–330. A high yield of polymeric products could be obtained by using ultraviolet light as initiator. The oxygen in the copolymer depends on the reaction temperature and the wavelength of the radiation used[20]. In the photochemical copolymerisation of perfluoropropene and oxygen at −60°C the copolymer $[-CF_2-CF(CF_3)-O-]_X$ is formed, but with increase in the copolymerisation temperature the number of peroxide groups in the copolymer decreases[21]. On heating or further irradiation the proportion of oxygen in the copolymer drops. Copolymers of this type contain reactive terminal –COF groups. The stability of the polyether can be greatly increased by converting the terminal acyl fluoride groups into carboxyl groups followed by decarboxylation of the latter. Oligomers of composition $[-C_3F_6-O-]_X$ exhibit high thermal and chemical stability. They are unchanged on heating to 350°C. The structure of the elementary unit of the polymer,

$$(-\underset{CF_3}{\underset{|}{CF}}-CF_2-O-),$$

was deduced from the ^{19}F NMR spectra and chemically[22].

2. Polymerisation of oxides and thio-oxides of fluorine-containing alkenes.

The polymerisation of oxides of fluorinated alkenes has been a more convenient method of making polyethers. It has allowed the process to be simplified and the formation of explosive peroxide polymers to be avoided. Oxides of the type

$$CF_3-CH\underset{O}{\diagdown\!\diagup}CH_2$$

have been polymerised in the presence of catalysts of the Lewis acid type[23] with the formation of a thermally stable polyether with $M \simeq 230\,000$. Peroxide initiators and γ-rays do not bring about polymerisation of this monomer[23]. Oligoethers with $M = 1000-4000$ were obtained from 2,3-epoxy-1,1,1-trifluoro-propane in the presence of anionic or cationic catalysts[24,25]. The nature of the terminal groups of the polyether depends on the polymerisation catalyst employed. The use of aluminium chloride as a catalyst facilitates the formation of terminal hydroxyl groups whereas when alkaline catalysts or boron trifluoride are used double bonds are formed as terminal groups[24]. High-molecular-weight polyethers are also formed from other oxides in the presence of cationic catalysts, for example, from epoxy-2,2,3,3-tetrafluoro-1-vinylbutane[26,27].

Active carbon[28–30], alkali metal fluoride[29,31], or γ-rays[32] have been used as catalysts for the polymerisation of perfluorinated oxides. The polyethers from perfluoro(epoxypropane) have the composition:

$$F-[C_3F_6O-]_x-\underset{CF_3}{\underset{|}{CF}}-COF.$$

To increase the stability of this polyether [30] or of the copolymer of perfluoroepoxypropane with epoxytetrafluoroethylene [33], the terminal –COF groups are decarboxylated. To do this, the polyether with terminal functional groups is treated with elemental fluorine and if double bonds are present ultraviolet light is used, which leads to doubling of the molecular weight of the polyether. If the ammonium salts of these acids are decarboxylated the polyethers will also contain rather stable $-CF_2H$ terminal groups [34].

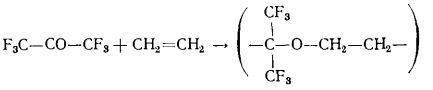
Fluorine-containing thio-oxides form homopolymers or copolymers in the presence of initiators of the radical type or under the action of ultraviolet radiation [35]. Fluorine-containing polythia-compounds exhibit increased fire resistance and chemical stability, and can also be used as plasticisers, for example, for poly(tetrafluoroethylene).

The polyethers from perfluoro(epoxypropane) exhibit extremely valuable properties [21] and are greatly superior to their non-fluorinated analogues. They are insoluble in various solvents, resistant to the action of oxidants such as O_2, O_3, and Cl_2 up to 250°C; stable to radiation, which distinguishes them favourably from poly(tetrafluoroethylene); incombustible, and of low toxicity. Liquid polyethers retain their viscosity over a wide range of temperatures and are used as lubricants. These polyethers withstand heating up to 410°C and low-molecular-weight polyethers can even be distilled at 490°C without decomposition. Films of fluorinated polyethers exhibit satisfactory mechanical strength and do not lose their elasticity at –80°C [36]. Attempts to use these polymers for obtaining rubbers were unsuccessful since no reliable methods for their vulcanisation have yet been discovered. The copolymerisation of perfluoroepoxyalkanes and perfluorodiepoxyalkanes (the preparation of the first representatives of fluorine-containing diepoxides and their polymers has been mentioned [37,38]), or the cross-linking of polyether macrochains at the stage of the decarboxylation of the terminal groups can probably be used for this purpose.

3. Copolymerisation of oxides and alkenes. Copolymers of fluorinated oxides and non-fluorinated alkenes are interesting. Perfluoroepoxyalkanes readily form block-copolymers with non-fluorinated vinyl monomers (styrene, butadiene, isoprene, methyl methacrylate, etc.) in the presence of alkali metals or their complexes with aromatic compounds [39]. Block-copolymers exhibit increased resistance to the action of organic solvents, increased impact strength, fire resistance, and low gas permeability. Fluorine-containing polyethers can also be obtained by the copolymerisation of non-fluorinated oxides, for example, ethylene oxide and highly fluorinated alkenes (perfluoropropene, chlorotrifluoroethylene) in the presence of peroxide initiators or on irradiating a mixture of monomers with ultraviolet light [40]. Copolymers soluble in organic solvents are formed thereby, and their composition and properties can be regulated readily by means of the composition of the initial mixture of monomers. Unlike poly(ethylene glycol), when exposed to the action of sulphuric acid at 150°C, the above copolymer is stable under these conditions.

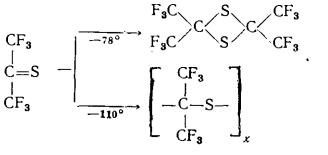
4. Polymerisation of ketones or thioketones and their copolymerisation with alkenes. The carbonyl groups of aldehydes and ketones are usually stable to the action of free radicals, although in some instances such reactions have been effected [41,42]. However, fluorinated ketones, the carbonyl group of which is under the inductive influence of electron-withdrawing perfluoroalkyl radicals, are capable of adding compounds of the R–H type at the carbonyl group under conditions for free-radical processes [43]. The carbonyl group of fluorinated ketones is reminiscent of the weakly polarised double bond of alkenes, which facilitates their participation in reactions which take place according to a free radical mechanism in comparison with non-fluorinated analogues. In the presence of t-butyl peroxide, hexafluoroacetone is capable of adding either simple low-molecular-weight substances (hydrocarbons, ethers, aldehydes, etc.) or high-molecular-weight compounds, for example, polyethylene [43]. It is noteworthy that fluorinated ketones are readily broken down into radicals under the influence of ultraviolet light. The least stable of them under these conditions is evidently hexafluorocyclobutanone. Even at room temperatures this loses the carbonyl group, being converted into perfluorocyclopropane [44]. At low temperatures hexafluorocyclobutanone polymerises in the presence of sodium acetate with the formation of a linear polyether.

Alkenes are readily copolymerised with hexafluoroacetone in the presence of peroxide initiators [45,46]:



Such copolymers exhibit reduced combustibility and water-repellant properties and can be used as protective coatings on metals. The copolymer of ethylene and hexafluoroacetone is sufficiently thermostable. When the copolymer has 11% hexafluoroacetone its loss in weight at 400°C is 1.5%, that at 470°C is 8.7%. The copolymer is readily formed into films [45]. Not only alkenes can undergo copolymerisation with polyfluorinated ketones, but also several other substances which do not form homopolymers (CO, SO_2, etc.). Such copolymers can be used for protecting metals, as adhesives for sheet materials, and for increasing the elasticity of polymers [47]. Polymeric fluorinated ketones copolymerise with polyalkenes, polyethers or polyamides, in the presence of peroxide initiators, improving the fire-resistance, adhesion, and dye receptivity of the latter [48]. However, nothing has been published on the possibility of vulcanising these copolymers.

Fluorine-containing thioketones readily undergo polymerisation both in the presence of special catalysts (boron trifluoride–diethyl ether, dimethylformamide, benzthiols [49,50], aluminium or titanium isopropoxides [51]) and without them [52]. The course of the reaction is greatly affected by the temperature. In the presence of dimethylformamide a dimer is formed from hexafluoroacetone at –78°C, whereas at –110°C the sole product of the reaction is a polymer of linear structure:



Thioketones with 5–10 carbon atoms polymerise with difficulty, forming dimers or liquid products. With decrease in the number of carbon atoms in the thioketone the polymerisation is facilitated and solid, high-molecular-weight polymers with comparatively moderate melting

points are formed. The polymers of fluorinated thioketones are of low stability: their depolymerisation takes place at −78°C [51,53] or at room temperature [50]. However, in some instances their stability is high, which allows elastic films or fibres, resistant to the action of solvents, to be obtained from them [49,52].

Hexafluoroacetone readily forms addition compounds of 1:1 composition with alkenes having an allyl hydrogen atom [54], which made possible the modification of natural polyisoprene [54] and other polydienes, such as polybutadiene and neoprene [55], with hexafluoroacetone. After such treatment the fluorine content of the polymer is 43%.

5. Polymerisation of aldehydes and thioaldehydes. Fluorine-containing aldehydes of the R_f-COH type polymerise extremely readily both in the presence of various catalysts or initiators and without them. For this reason it has been impossible to determine the precise boiling point of thioacetaldehyde, as this polymerises during distillation [56,57]. The polyether formed as a result of the spontaneous polymerisation of the fluoral melts at ~50°C and depolymerises on heating. During a more detailed investigation of the conditions for the polymerisation of fluorinated aldehydes certain regularities were found [58]. In the polymerisation of the lower aldehydes peroxide initiators were more active than acid catalysts (H_2SO_4, Ac_2O). The higher fluorinated aldehydes polymerise more easily under the action of acid catalysts.

The structure of poly(fluoroaldehydes) is that of substituted poly(oxymethylenes) with terminal hydroxyl groups. Their thermal stability can be enhanced by replacing the terminal hydroxyl groups by halogen [59]:

$$HO-\underset{R_f}{CH}-\left[O-\underset{R_f}{CH}\right]_x OH + SOCl_2 \rightarrow Cl-\underset{R_f}{CH}-\left[O-\underset{R_f}{CH}\right]_x-Cl$$

Polyaldehydes containing fluorine and chlorine atoms, for example, poly(chlorodifluoroacetaldehyde), are less stable to the action of elevated temperatures than poly(perfluoroaldehydes) [60] and are depolymerised even at 180°C, forming the monomeric aldehyde.

Poly(fluoroaldehydes) can be used as coatings for metals. They are insoluble in organic solvents, oligophobic and hydrophobic, and do not decompose in contact with fuming nitric acid, or boiling alkalis, but break down in boiling sulphuric acid. Their depolymerisation was observed at 380−400°C, but other studies gave a considerably lower depolymerisation temperature [57,60].

Copolymers of formaldehyde and fluorinated aldehydes are very interesting. The copolymerisation of these monomers proceeds at low temperatures in the presence of quaternary ammonium salts [61]. After protection of the terminal hydroxyl groups a sufficiently stable polymer, which exhibits good mechanical properties in the temperature range from −78° to +200°C, is obtained.

Fluorine-containing polythia-compounds can be obtained readily by the polymerisation of such fluorine-containing thiocarbonyl compounds as thioaldehydes or thioacyl halides. In certain instances the polymerisation of these compounds proceeds spontaneously [62]. Thiocarbonyl fluoride is the simplest monomer which can be used for this purpose. It can be polymerised both by anionic [63,64] and by free-radical [65] mechanisms. Dimethylformamide [50,63], titanium or aluminium isopropoxides [63,64], and boron trifluoride−diethyl ether [50] have been used as catalysts for the polymerisation of thiocarbonyl compounds. Ultraviolet light [65,66] or organoboron compounds in conjunction with oxygen or oxidants [65] can be initiators of the free-radical polymerisation of fluorothiocarbonyl compounds.

Poly(thiocarbonyl fluoride) with $M = 2000-5000$ is formed even on storage of the monomer [50]. In the presence of catalytic amounts of dimethylformamide at −78°C thiocarbonyl fluoride is readily converted into a polymer of structure $[-CF_2-S-]_x$. The initiation of the anionic polymerisation of thiocarbonyl fluoride, chain growth, and chain breaking can be represented by the following scheme:

$$CF_2=S \xrightarrow{\text{solvent}} (CF=S)^+ + F^- + CF_2=S \rightarrow CF_3-S^-;$$
$$CF_3-S^- + CF_2=S \rightarrow CF_3-S-[CF_2-S]_x-CF_2-S^-;$$
$$CF_3-S-[CF_2-S-]_x CF_2-S^- \rightarrow CF_3-S-[CF_2-S]_x-CF=S + F^-.$$

This polythia-compound contains terminal thiocarbonyl groups −CF=S and a small number of −CF=O carbonyl groups, observable in the infrared spectrum of the polymer [50]. The value of the characteristic viscosity, measured for a 0.1% solution of the polymer in chloroform, varied from 3 to 6 [50,64], and the molecular weight, determined by an osmometric method, reached 300 000−400 000 [67]. Poly(thiocarbonyl fluoride) is an elastic and hard polymer, m.p. ~35°C, glass point −118°C, decomp. temp. 175°C. It can readily be formed into films (σ = 770 kgf cm^{-2}, ϵ = 90%). This polymer is stable to the short-time action of boiling nitric acid and boiling solutions of alkalis. Under the action of amines, poly(thiocarbonyl fluoride) is destroyed very rapidly [63]. Alkali brings about the slow destruction of this polythia-compound by acting on the terminal groups. The ability of the polymer to withstand high temperatures and alkalis can be considerably increased by conversion of the terminal thiocarbonyl groups into trifluoromethyl groups. To do this the polymer is treated with antimony(V) fluoride [50], after which the resistance of the polymer to the action of amines is also increased:

$$CF_3-S-[CF_2-S]_x-CF=S \xrightarrow{SbF_5} CF_3-S-[CF_2-S-]_x-CF_3$$

Another method of increasing the stability of this type of polythia-compound to the action of heat or amines is the copolymerisation of thiocarbonyl fluoride with certain halogenated thioacyl fluorides [63], for example, with CHFCl−CF=S. It is interesting to note that the homopolymers of thioacyl fluorides [51] are destroyed by alkalis even at room temperature [50].

The higher fluorinated thioaldehydes readily polymerise with the formation of liquid or solid high-molecular-weight compounds [68]. Crystalline polythia-compounds with branched fluorinated radical, which reduces their solubility in organic solvents, were obtained in the polymerisation of fluorinated thiobutyraldehyde [69]:

$$(CF_3)_2CF-CHS \rightarrow \underset{\underset{CF(CF_3)_2}{|}}{[-CH-S-]_x}$$

The decomposition temperature of this polymer is ~200°C.

A series of copolymers of fluorinated thiocarbonyl compounds with other monomers has been obtained. Elastomers which do not crystallise at low temperatures are formed in the copolymerisation of thiocarbonyl fluoride with various alkenes [70] (ethylene, but-2-ene, styrene, butadiene, vinyl fluoride). These copolymers are more resistant to thermal destruction and are fabricated more readily. Copolymers of thiocarbonyl fluoride are extremely resistant to the action of concentrated nitric acid [66]. To reduce the tendency towards crystallisation of poly(thiocarbonyl fluoride) it was copolymerised with a thioacyl fluoride in the presence of catalytic amounts of aluminium or titanium alkoxides [71].

5. Aromatic polyethers and polythia-compounds. In the preparation of *p*-trifluoromethylphenol it was noted that in an alkaline medium in the cold it is converted into a polymer of structure $[-CF_2-C_6H_4-O-]_x$ [72]. Potassium perfluoro-*p*-tolyl oxide was more stable under these conditions; its polycondensation in the cold was very slow. At elevated temperatures a polyether with $M = 1500-3000$ is formed[73]:

$$CF_3-C_6F_4-OK \rightarrow [-CF_2-C_6F_4-O-]_x$$

Such a structure was attributed to the polyether from the ^{19}F NMR spectra. This polyether melts at ~100°C and starts to decompose at ~300°C.

A number of aromatic polyethers are of great interest. The tendency of perfluorinated aromatic compounds to undergo nucleophilic substitutions has been utilised for their preparation. When hexafluorobenzene is heated with alkalis, alkali metal pentafluorophenoxides are formed and on further heating they are converted into polyethers:

$$C_6F_5OK \rightarrow C_6F_5\ O-[C_6F_4-O-]_x-C_6F_4-OK$$

The softening temperature of poly(perfluoro-*p*-phenylene oxide) with $M \simeq 12\,000$ exceeds 100°C.[74]

Poly(perfluoro-*p*-phenylene sulphide), which melts at temperatures above 300°C, was obtained by the same scheme. Its structure is clearly shown by its desulphidation on Raney nickel, which gives only 1,2,4,5-tetrafluorobenzene (structural units) and a little pentafluorobenzene (terminal units).

However, the thermal stability of these polyethers and polythia-compounds was less than that of their non-fluorinated analogues. A similar relation was also noted in investigating the thermal destruction of the perfluoropolyphenylenes[75]. Evidently, the introduction of fluorinated phenyl nuclei into the chains of the polymers does not give a product more stable thermally than its non-fluorinated analogue. The presence of terminal hydroxyl or phenoxide groups should also facilitate subsequent processes which are accompanied by the release of alkali metal fluorides or of hydrogen fluoride.

B. Carbochain Polyethers and Polythia-compounds

There have been many publications, mainly patent specifications, describing polyethers obtained by the polymerisation of vinyl or allyl ethers and also of glycide ethers, that is, polyethers in which the oxygen atoms are in side-chains. Fluorine atoms were introduced into the alkyl (aryl) or vinyl part of these monomers or in both parts simultaneously.

1. Polymers and copolymers of fluoroalkyl vinyl or allyl ethers. This section will consider polymers made from monomers of structure $R_f-O-CH=CH_2$ or $R_f-CH_2-O-CH=CH_2$. The polymerisation of the non-fluorinated double bond of this type of monomer can be brought about by initiators of free-radical processes or catalysts of ionic type. The ability to polymerise under conditions of free-radical initiation depend on the structure of the original monomer. Perfluoroisopropyl allyl ethers[76] or $\alpha\alpha$-dihydroperfluoro-*n*-alkyl vinyl ethers[77] can be polymerised in the presence of benzoyl peroxide or ultraviolet light, whereas pentafluorophenyl vinyl ether does not polymerise[78] in the presence of free-radical initiators. It is noteworthy that the polymerisation of fluoroalkyl vinyl ethers has been studied insufficiently. There have been contradictory statements about the ability of peroxide initiators to bring about the polymerisation of some of these monomers[79]. In recent studies it has been noted[80] that the catalysts mentioned in earlier studies are either inactive generally or exhibit a very low activity.

In this respect fluoroalkyl vinyl ethers are reminiscent of their non-fluorinated analogues, which under the action of light or of initiators of the free-radical processes are slowly polymerised with the formation of low-molecular-weight products.

Catalysts of the Friedel–Crafts type are more effective for the polymerisation of fluoroalkyl vinyl ethers (as for their non-fluorinated analogues. Aluminium chloride[78], boron trifluoride–diethyl ether[77,80-82], or gaseous boron trifluoride[78,80] at low temperatures have been used as such catalysts. The polymerisation rate and the molecular weight of the polymer depend on the type of catalyst. Evidently, the most active is gaseous boron trifluoride; when this is used, trifluoroethyl vinyl ether is polymerised very rapidly with the formation of a high-molecular-weight product, whereas with boron trifluoride–diethyl ether the polymerisation is slow and a low-molecular-weight polyether is formed [80].

The presence of fluorinated substituents as side-chains confers a series of valuable properties upon the polymer: fire resistance, water- and oil-repellance, which enables it to be used as protective coatings for metals, cloth, paper, etc. An extremely interesting property of such polyethers, especially polyethers obtained from monomers with branched fluorinated radicals, is the extremely small critical surface tension for wetting. For example, for poly(heptafluoroisopropyl vinyl ether) $\gamma_w = 14.2$ dyne cm^{-1} [79]. It has been proposed to use a series of fluorine-containing polyethers as adhesives, like their non-fluorinated analogues[77].

Copolymers of fluoroalkyl vinyl ethers with various vinyl monomers are interesting. The copolymerisation can be carried out blockwise, in emulsion, or suspension in the presence of initiators of free-radical polymerisation[83]. Lauryl peroxide[84] or redox systems based on ammonium persulphate[85-87] have been used as polymerisation initiators. Usually, in the copolymer there is a smaller amount of the fluoroalkyl vinyl ether than there was in the monomer mixture[84]. The presence of polyfluoroalkoxide substituents in the copolymer chain increases the plasticity of the polymers. Copolymers of trifluoroethyl vinyl ether and tetrafluoroethylene can be fabricated into articles by the usual methods[85]. The introduction into the polyvinyl chloride chain of this same monomer increases its thermal and chemical stability which allows these copolymers to be used for protective coatings for metals[85]. Even small quantities of trifluoroethyl vinyl ether give its copolymers with vinyl chloride and other vinyl monomers increased thermal stability and improve their resistance to attack by solvents[84,86]. The use of these monomers for the preparation of special-purpose rubbers can be extremely promising. Copolymers of perfluorobutadiene and poly(fluoroalkyl vinyl ethers) compounded with carbon black are readily vulcanised with the formation plastics which withstand oil and petrol. Their resistance to oxygen at high temperatures is higher than that of rubbers based on copolymers of non-fluorinated butadiene and acrylonitrile[87]. Vinyl ethers, especially those which also contain other functional groups, for example, the ethylvinyl ether of 2-*N*-ethylperfluorooctanesulphonamide are used for the special treatment of fabrics to confer on the latter resistance to oil and water[88].

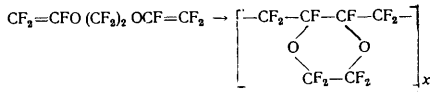
3. Polymers and copolymers of alkyl-perfluorovinyl and allyl ethers and sulphides. Unlike vinyl ethers with a non-fluorinated double bond, perfluorovinyl ethers are readily polymerised in the presence of initiators of free-radical processes. The following initiators were used for the polymerisation of these monomers: benzoyl peroxide[89], γ-radiation[90], or tetrafluorohydrazine[91]. Perfluorovinyl sulphides do not polymerise in the presence of benzoyl peroxide[89]. In the general case the ability of these monomers to polymerise decreases in the order[90]:

$$R_f{-}CH_2{-}O{-}CF{=}CF_2 > R_f{-}O{-}CF{=}CF_2 > R_f{-}S{-}CF_2{=}CF_2 .$$

The molecular weight of the polymers changes in the same order. It is noteworthy that the sulphides $R_f{-}S{-}CF{=}CF_2$ not only polymerise badly themselves but also inhibit the polymerisation of other vinyl monomers[90], probably because of capture of the electron by the vacant orbital of the sulphur atom. Polyethers of fluorine-containing allyl ethers were obtained from the corresponding monomers in the presence of persulphates[92]. They are used as adhesives for attaching halogenated polymers to metals.

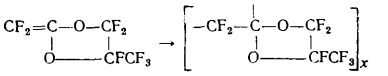
Alkyl- and polyfluoroalkyl-perfluorovinyl ethers are readily copolymerised with various vinyl monomers[93] to form liquid or solid copolymers[89]. High-melting copolymers of perfluoromethyl vinyl ether with tetrafluoroethylene can be converted into articles by the usual methods, for example, into stiff colourless and transparent films[90,91]. High-molecular-weight copolymers are formed when perfluoropropyl vinyl ether and tetrafluoroethylene are polymerised together[94,95]. The preparation of copolymers with various fluorine-containing alkenes is of interest for the production of elastomers with increased thermal stability and excellent resistance to frost. For example, a copolymer of vinylidene fluoride and perfluoroethyl vinyl ether, strengthened with magnesium oxide and hexamethylenediamine, retains its flexibility at $-25°C$ and its loss in weight after 200 h at 288°C totalled 10%[96]. Such materials were proposed for use for fuel cells and diaphragms working in contact with liquid fuel.

Perfluorinated bisvinyl ethers of the type $CF_2{=}CFO[CF_2]_n{-}OCF{=}CF_2$ are polymerised or copolymerised with fluorine-containing alkenes block-wise, in solution, or suspension in the presence of peroxide-type initiators. These monomers are interesting because their polymerisation can be effected at one vinyl group and then the fore-polymer obtained is converted into a cross-linked product by subsequent polymerisation in moulds[97]. In the polymerisation of such monomers ($n = 2$) in the presence of peroxides, for example, peroxides of the $(C_3F_6O_2)_x$ type[98], polyethers with rings in the chain are formed[99]:

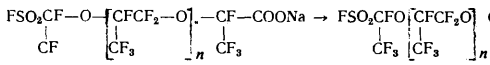


these exhibit high chemical stability and good electrical insulating properties. They are thermoplastic and can be extruded or cast under pressure. These polyethers withstand boiling nitric and sulphuric acids and boiling alkali solutions. Perfluorodivinyl ethers copolymerise with perfluoroalkyl vinyl ethers or perfluoroalkenes to give a fore-polymer. After additional polymerisation a rigid, chemically inert material is obtained[100].

The polymerisation of perfluoro-4-methyl-2-methylene-1,3-dioxolane in the presence of tetrafluorohydrazine gave a polymer with unusually high gas permeability[101], which allowed it to be used for the separation of many gases:

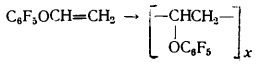


Perfluorovinyl ethers with several ether bonds are obtained by the pyrolysis of the alkali salts of carboxylic acids[102]:

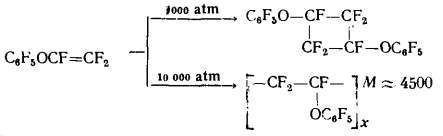


Polymers or copolymers of these vinyl ethers with vinylidene fluoride are plates or elastomers.

Of the fluorine-containing vinyl ethers, that with the least ability to polymerise is probably the phenyl vinyl ethers. Pentafluorophenyl vinyl ether[103] and its derivatives which contain a single hydrogen atom in the vinyl group[104] can be polymerised in the presence of Friedel-Crafts type catalysts. The molecular weights of these polymers are low (2300–17 000), and their melting points lie in the range 120–180°C.



Phenyl perfluorovinyl ethers[105] or perfluorophenyl vinyl ethers[106] are polymerised with difficulty even at 230°C after 10 days[107], the yield of polymers with characteristic viscosity 0.03 totalling 2–3%. However, on irradiation of these monomers with γ-rays at high temperatures a polyether soluble in perfluorobenzene and of increased thermal stability could be obtained in 6–7% yield. These monomers were polymerised by using high pressure (10 000 – 15 000 atm [106]) since at a pressure of 1000 atm dimers are formed exclusively:



3. Polymerisation and copolymerisation of glycide ethers. Fluoroalkyl glycide ethers became available monomers after the ability of perfluoroketones to react with alkali metal fluorides to form alkoxides of perfluoroalcohols had been observed. When the latter react with epichlorhydrin or epibromohydrin they are converted into the corresponding glycide ethers[109,110]. Glycide ethers based on hexafluoroacetone are polymerised in the presence of catalytic amounts of water and diethylzinc at $-70°C$ [109], whereupon a highly elastic polymer with $M \simeq 84\,000$, insoluble in ordinary and soluble in fluorinated solvents is formed[110]. The glass point and decomposition temperature of these polymers are $-43°$ and $+270°C$ respectively. When the glycide ethers are polymerised in the presence of boron trifluoride–diethyl ether, low-molecular-weight liquid products were isolated. Homopolymers and also copolymers of these monomers with the oxides of other alkenes are used for obtaining resins, coatings, adhesives, and also for special treatment of fabric to confer oil- and water-repelling properties upon it. For impregnation of overalls, glycide ethers of pyrans are also used[111], the polymerisation of which is effected in the presence of iron(III) chloride. Thermoreactive resins are obtained from glycide ethers, the molecules of which contain an additional vinyl group[112].

These resins were hardened by using amines, for example, diethylenetetramine. Perfluorinated epoxyalkenes of structure

$$CF_2=CF[CF_2]_n-CF-CF_2$$
$$\qquad\qquad\quad \backslash O /$$

are of considerable interest[113]. Monomers of this type can be polymerised or copolymerised with various fluorinated alkenes or their oxides to form polyethers capable of being hardened by polymerisation of the second functional group. These polymers have high thermal and chemical stability and can be used to obtain fibres, films, and moulded articles.

4. Modification of celluloses by fluoride-containing compounds. There have been descriptions of attempts to introduce fluorine atoms into cellulose or manufactured articles made on its basis. Attempts were made to introduce isolated fluorine atoms into cellulose by the action of the tosyl ethers of alkali metal fluorides upon it[114]. This method gives good results with several of the simplest esters of toluenesulphonic acids, but only small quantities of fluorine could be introduced into cellulose by this method. A method based on reactions of nucleophilic addition of alcohols to perfluoroalkenes, for example, to perfluoropropene, was more effective[115]. In alkaline medium cellulose reacts with perfluoropropene to form ethers of the $R-O-CF_2-CFH-CF_3$ type and a certain amount of ethers of the $R-O-CF_2-CF=CF_2$ type, products of the substitution of fluorine atoms in the allyl position. The ether bonds of such types were stable in acid and alkaline media, probably because of the increase in the hydrophobic nature of such fluorine-containing polymers. Up to 13% fluorine could be introduced into cellulose by this method and the polymer itself acquired water-repelling properties. Other fluorinating media can be used for introducing fluorine atoms, for example, sulphur tetrafluoride[116]. This fluorinating agent readily replaces hydroxyl, carbonyl, or carboxyl groups by fluorine atoms with the formation of C–F, CF_2, or CF_3 groupings respectively. This method is suitable for making paper or cardboard water-repellent.

III. POLYESTERS

Nonfluorinated polyesters are readily formed in reactions between dicarboxylic acids and diols or polyols. In several instances re-esterification between the dimethyl or other diethers of dicarboxylic acids and diols has been used successfully. In certain instances (mainly in working with diols with increased acidic properties, for example, with various bisphenols) acyl halides of dicarboxylic acids are used. Polyesters are interesting for obtaining fibres, films, etc. or are intermediates for further syntheses, for example, for obtaining polyurethanes, etc.

In comparison with carboxylic acids their fluorinated analogues are stronger. The dissociation constant of acetic acid is 1.8×10^{-5}, whereas that for trifluoroacetic acid is several orders of magnitude greater (5.9×10^{-1}). This strengthening of the acidic properties is due to the inductive influence of the electron-withdrawing fluorinated radical. A similar effect of fluorinated radicals is seen in the acidic properties of fluorine-containing alcohols. Alcohols with the $-CF_2OH$ grouping are unknown. Alcohols with $-CF_2CH_2OH$ groups are completely stable. They are obtained in the telomerisation of tetrafluoroethylene and methanol (monohydric alcohols) or in the reduction of diesters of perfluorodicarboxylic acids (diols). The acidic properties of 1,1-dihydroperfluoro-alcohols are comparable with those for phenols. Therefore the direct esterification of such alcohols is difficult. To obtain esters under such conditions the anhydrides or acyl halides of fluorinated or non-fluorinated carboxylic acids are used.

The polyethers obtained from dicarboxylic acids and diols and also the polyesters made by the polymerisation of unsaturated esters are of practical interest. Both types of fluorine-containing polyester will be considered below.

A. Heterochain Polyesters

The available aliphatic fluorine-containing dicarboxylic acids at present are perfluoroadipic and perfluoroglutaric acids. They are obtained by the oxidation of dichlorooctafluorocyclohexene or dichlorohexafluorocyclopentene respectively. The electrochemical fluorination of dicarboxylic acids to perfluorodicarboxylic acids is extremely promising. Despite the comparatively low yields of valuable products (up to 20%) the electrochemical fluorination is simple and allows the process to be effected in a single stage. The preparation of the higher perfluorodicarboxylic acids is extremely difficult, which hinders the investigation of these products as monomers at present. Dimethyl or diethyl perfluorodicarboxylates are readily reduced to $\alpha\alpha\omega\omega$-tetrahydroperfluoroglycols of the type $HOCH_2[CF_2]_nCH_2OH$. Diols with $n = 3$ and 4 were used to obtain polyesters.

1. Polyesters from dicarboxylic acids and diols. Fluorine-containing polyesters have been studied in sufficient detail for some of them to be put into industrial production, whereas poly(thioesters) have hardly been investigated at all. The preparation of poly(thioesters) from the anhydrides of perfluorodicarboxylic acids and of non-fluorinated dithiols have been mentioned in the literature, but the properties of the polymers were not given[117].

Fluorine-containing polyesters can be obtained by all the methods employed for the preparation of their non-fluorinated analogues. However, high molecular weights could not always be attained. Polyesters with moderate molecular weights are readily formed from the anhydrides of perfluorodicarboxylic acids and fluorinated diols[118]. High-molecular-weight polyesters also could not be obtained by heating the disilver salts of perfluorodicarboxylic acids with $\alpha\omega$-polymethylene di-iodides[119] or by the esterification of non-fluorinated diols with perfluorodicarboxylic acids[119].

Best results were obtained on using the bisacyl chlorides of perfluorodicarboxylic acids. When the latter were heated with fluorinated diols polyethers with molecular weights up to 17 000 could be obtained[120]. Polyethers with even higher molecular weights are formed on using bis(acyl chlorides) of non-fluorinated dicarboxylic acids[121]. Polyesters can be obtained by re-esterification between the dimethyl esters of non-fluorinated dicarboxylic acids and fluorinated diols. Alkali metal alkoxides, metal oxides, and strong acids have been used as catalysts for the re-esterification[122]. The second stage (polycondensation) takes place at 200–300°C in the presence of catalytic amounts of oxides of Sb, Bi, Ti, or Mg.

Aliphatic or aromatic dicarboxylic acids can be used as the acidic constituent. Aliphatic dicarboxylic acids form low-melting or liquid polyesters[117-120], which exhibit high thermal stability and elasticity at low temperatures. Their glass points lie in the range from −30° to −57°C. Such polyesters are capable of being cross-linked at the stage of their preparation with polyols (glycerol)[120], or at the stage of subsequent retreatment with peroxides or calcium carbonate[121], or by other functional groups, for example, hydroxyl groups, found in the dicarboxylic acid molecule[122]. One of the most valuable polyesters of this type is poly(hexafluoropentamethyleneadipate). The oil- and petrol-resistant rubbers from this polyester, which exhibit good low-temperature characteristics, are produced on an industrial scale[123,124]. They can be used at temperatures from −72° to +150°C. Despite the fact that their mechanical properties are not outstanding (σ = 160 kgf cm^{-2}, ϵ = 120−230%), these rubbers have found practical application in the aviation industry.

Attempts have been made to increase the thermal stability of aliphatic polyethers by using terephthalic acid in place of part of the adipic acid. The resistance of low-molecular-weight polyesters ($M \simeq 1800-2700$) to heating was improved to some extent by replacing 30% of the adipic acid by terephthalic. The other properties of the polyesters changed insignificantly[125]. A further increase in the proportion of terephthalic acid leads to an increase in the melting points of the mixed polyester and a deterioration in its low-temperature characteristics[126]. Polyesters based on terephthalic acid and fluorinated diols are plastics themselves; they are readily soluble in organic solvents and are used as heat-resistant protective coatings or as cast resins[127].

In certain instances, when both the acid and diol are fluorinated, it is desirable to introduce a certain proportion of non-fluorinated diol or non-fluorinated hydroxy-acid into the polyester. These additions favour an increase in the molecular weights of the polyesters[128].

All the aliphatic fluorine-containing polyesters undergo hydrolysis to a considerable extent. Their hydrolytic stability is considerably less than that of their non-fluorinated analogues.

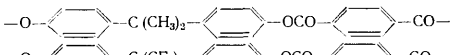
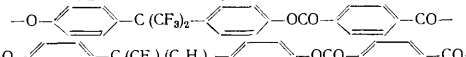
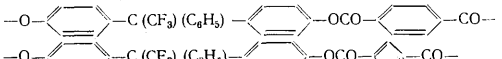
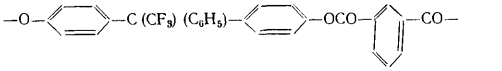
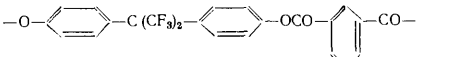
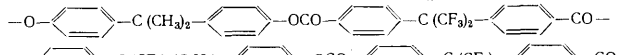
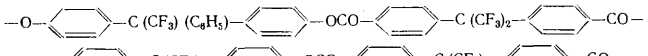
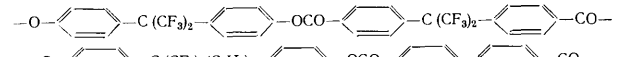
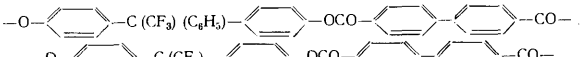
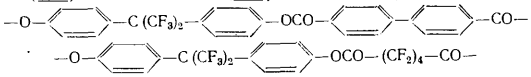
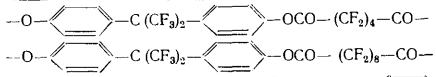
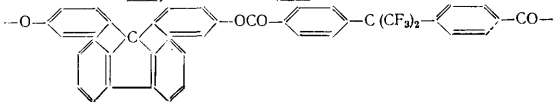
2. Polyesters from fluorinated aromatic dicarboxylic acids. Nothing has been published about polyesters obtained from aromatic dicarboxylic acids having fluorinated phenyl nuclei. Only the use of fluorophthalic anhydride for the preparation of glyptal resins has been described[129]. Evidently, the use of fluorinated aromatic dicarboxylic acids for the preparation of polyesters does not lead to an increase in their thermal and hydrolytic stabilities. The fluorine atoms, like those of any other halogen, will be comparatively easily displaced by nucleophilic agents under the influence of electron-withdrawing carboxyl groups even during the preparation of polyesters at 150−200°C. Furthermore, fluorinated aromatic acids themselves are readily decarboxylated on heating. Pentafluorobenzoic acid starts to decompose even at 190°C, and tetrafluoroisophthalic acid is decarboxylated at 203°C [130].

There is also considerable interest in aromatic dicarboxylic acids in which the fluorine atoms are not in the phenyl nuclei but in the side-chains. The acids of this type are devoid of the above drawbacks. Their thermal and chemical stabilities should be close to those for benzoic and terephthalic acids. The recently synthesised dicarboxylic acids of the type $HOOC-C_6H_4[CF_2]_n-C_6H_4COOH$ [131,132] and acids of the type $HOOC-C_6H_4-C(CF_3)_2-C_6H_4COOH$ can be regarded as promising monomers for the preparation of fluorine-containing polyesters. The latter acids have already been used for the preparation of polyesters[133]. The diols were aliphatic fluorinated diols or bisphenols of aromatic or aliphatic−aromatic series. The bis(acyl chlorides) of the dicarboxylic acids and bisphenols form polyesters (polyarylates) under interphase polycondensation conditions[134]. Table 1 gives certain properties of the fluorine-containing polyarylates with those their non-fluorinated analogues for comparison. As Table 1 shows, the replacement of methyl groups at the central atom of the bisphenol by trifluoromethyl groups leads to some increase in the thermal stability of the polyesters. Fluorine-containing polyarylates exhibit greater elasticity than their non-fluorinated analogues and are readily converted into films with satisfactory strength characteristics. Their breaking strength reaches 700−1000 kgf cm^{-2} and the elongation is 30−70%. Polyesters made from bisphenols fluorinated in the aromatic nucleus decompose at ~300°C [140].

A detailed study of the kinetic features of the thermal degradation of polyesters based on adipic, fumaric, or terephthalic acid and octafluorohexane-1,6-diol was made at 260−420°C. The replacement of part of the adipic acid by isophthalic acid in the preparation of the polyesters, or the use of fumaric acid, did not lead to an improvement in the thermal stability of the polyester[141]. A considerable increase in the thermal stability was noted for polyesters based on terephthalic acid. The release of volatile degradation products was observed here at 360−380°C, whereas polyesters from aliphatic acids released gaseous products at much lower temperatures (220−260°C). It is interesting to note that the hydrogen fluoride or silicon tetrafluoride formed in the reaction of the latter with glass were not observed in the degradation products[142]. The temperature for the start of the degradation of the fluorine-containing polyester based on terephthalic acid exceeds these values for poly(chlorotrifluoroethylene) and copolymers of vinylidene fluoride with chlorotrifluoroethylene or perfluoropropene and also for poly(ethylene terephthalate) for which degradation in nitrogen atmosphere was observed even at 280−320°C. A similar series of relations was also found for the degradation of fluorine-containing polyesters in the presence of oxygen[143], but the temperatures at which the polymer loses 25% of its weight in oxygen atmosphere is lower than for the same temperatures in a vacuum.

3. Polyesters based on carbonic acid (polycarbonates). Non-fluorinated polycarbonates have found application for the production of fibres, films, etc. There have been few studies of fluorinated polycarbonates. Aliphatic fluorine-containing polycarbonates were made from octafluorohexane-1,6-diol and octafluorohexamethylenebis(chloroformate) in the presence of an acceptor of hydrogen chloride[144]. This polycarbonate has a lower melting point than its non-fluorinated analogue, but it is 7−8 times more resistant to heating and hydrolyses somewhat more slowly in acid medium than the same non-fluorinated polycarbonate. Mixed polycarbonates of hexafluoropentane-1,5-diol and 2,2-bis-(*p*-hydroxyphenyl)-propane exhibit high chemical stability, good dielectric and water-repellant properties, and low coefficients of friction[145]. Polycarbonates from fluorinated aromatic bisphenols are obtained by interfacial polycondensation. Some improvement in the physicochemical characteristics of polycarbonate can be brought about by the introduction of individual fluorine atoms into the aromatic nuclei of the

Table 1. Thermal characteristics of fluorine-containing polyesters.

Structural unit of the polyester	T_{decomp}, °C	T, start of decompn. in nitrogen, °C	T for 20% weight loss in nitrogen, °C	References
	350	397	462	135
	261.350	438	512	134, 135, 136
	290.310	446	482	134, 135, 137
	260.300	—	—	134, 137
	240.290	—	—	134, 137
	280.300	424	484	135
	300	—	—	138
	280	424	484	135
	320	—	—	139
	400	—	—	139
	120	—	—	134
	80	—	—	134
	340	458	484	135

bisphenol. For example, the replacement of hydrogen atoms by fluorine in the *ortho*-position to the hydroxyl group of 2,2-bis(*p*-hydroxyphenyl)propane improves its Vik heat resistance from 164–166° to 170–175°C, and appreciably increases its volume resistivity in comparison with its non-fluorinated analogue[146,147]. However, the mechanical characteristics of the polymers and their melting points are almost unchanged, although the flame resistance of the fluorinated polycarbonates is improved.

The melting point of a polycarbonate can be raised considerably by substituting fluorine for the hydrogens of the methyl groups in the bisphenol molecule. The polycarbonate based on 2,2-bis(*p*-hydroxyphenyl)-1,1,3,3-tetrafluoro-1,3-dichloropropane melts at 295–315°C [147], whereas the melting point of crystallites of its non-fluorinated analogue is 263°C [147]. Polycarbonates of this type are distinguished by increased heat resistance and low steam permeability.

B. Carbochain polyesters

Methods of preparation and certain physicochemical properties of fluorine-containing polyesters in which the ester grouping is found in the side-chain of the polymer will be considered in this section. Polyesters of this type are of great practical interest. The starting monomers for certain types of carbochain polyesters are now available on an industrial scale. Their polymerisation, further treatment, and vulcanisation is carried out by the usual equipment of the synthetic rubber industry. Oil- and petrol-resistant rubbers with good frost resistance are processed on an industrial scale.

1. Polymers and copolymers of acrylic and methacrylic acids. Non-fluorinated esters of acylic or methacryllic acids are readily polymerised with other vinyl monomers in the presence of initiators of free-radical type. Esters of fluorinated acrylic acid polymerise badly under these conditions. Yakubovich and coworkers[148] explain such a sudden decrease in the activity of these monomers by the presence of a double bond conjugated with a carbonyl group in molecules of the type $CF_2=CF-COOR$, which leads to the formation of radicals of low activity and hinders the homopolymerisation of these esters. In the presence of other non-fluorinated vinyl monomers the esters of perfluoroacrylic acid form copolymers with high molecular weights. The introduction of fluorine atoms into the methyl group of methacryllic acid has little effect on the reactivity of the monomers but somewhat reduces the decomposition temperature of these polymers in comparison with their non-fluorinated analogues[149].

There is great interest in polymers obtained from esters of acrylic acid and fluorinated alcohols. These monomers readily polymerise spontaneously[150] or in the presence of various initiators: the light of an incandescent lamp[151], benzoyl peroxide[150,152,153], the lauryl[150] or acetyl[150] radicals, azoisobutyronitrile[150], ultraviolet light[150,154], high-energy electrons[155], hydrogen peroxide[152], aqueous solutions of potassium[151,152,156,157] or sodium[151,158,159] persulphate in the presence of various emulsifiers. The polymerisation of 1,1-dihydroperfluoroalkyl acrylates can be effected blockwise, in solution, or in emulsion[160]. Emulsion polymerisation is the most convenient method of polymerisation of such monomers. The molecular weight of the homopolymers reaches 10 000 000. The low-temperature properties, and also their resistance to swelling, depend considerably on the structure of the monomers. The glass points of the fluorine-containing polyesters are higher than those of their non-fluorinated analogues. The glass points in the polyfluoroalkylacrylates depend on the number of difluoromethylene groups in the alcohol residue.

They fall gradually and reach a minimum for the polymer with an alcohol residue with 6 carbon atoms. The polymer with 8 carbon atoms in this residue is already crystalline. It is interesting to note that in the series of non-fluorinated acrylates crystallisation is observed only for those polymers, the alcohol residues of which consist of 14 or more carbon atoms[161]. Nothing has been published on the minimal glass point for non-fluorinated acrylates, but the values for the brittle points[162] suggest that it will be for the polymer with an alcohol residue with 8 carbon atoms. The segment length for 1,1-dihydroperfluorobutyl acrylate, polymerised in the presence of potassium persulphate, has been found to be 15 carbon atoms[163]. This exceeds the values for other elastomers (seven carbon atoms for polyisobutene, eleven for polystyrene), but could not be connected with the glass point.

The frost resistance of fluoroalkyl acrylates was increased by the introduction of an ether bond into the chain of the alcohol residue.[164,165] Side-radicals with an ether bond increase the flexibility of the polymeric chain, playing the part of a plasticiser.

The resistance of these polymers to swelling in organic solvents also depends on the number of fluorine atoms in the alcohol residue and is rather high for a large degree of fluorination of the latter.

The most valuable polymers are those from 1,1-dihydroperfluorobutyl acrylate which have been named 1F4, or polyFBA [166-168], and the polymers from 3-(perfluoromethoxy)-1,1,-dihydroperfluoropropyl acrylate, called 1F2. These polymers were vulcanised by all the methods used for the vulcanisation of polyester rubbers. When the salts, oxides, or hydroxides of bivalent metals are used as vulcanising agent, these polyesters acquire increased mechanical strength. The use of magnesium oxide has maximal effect. In the vulcanisation of fluoroacrylate polyesters by polyamines[165,169,170] the vulcanisate acquires a resistance to the action of high temperatures, mineral acids, and oxygen. The vulcanisation of polyesters by the above agents evidently proceeds by the formation of salt bridges between the carboxyl groups which appear as a result of the hydrolysis of ester groups, and by bivalent metals owing to the formation of amide bridges. Strongly alkaline agents, for example, sodium silicate[165,169], can bring about ester condensation, which also leads to cross-linking of the macro-chain of the polyester.

Certain properties of 1F4 and 1F2 resins are given in Table 2.

Fluorinated rubber of grade 1F4 exhibits high resistance to the action of organic solvents of various classes (aliphatic and aromatic hydrocarbons, chlorinated hydrocarbons, ketones, etc.) which allows them to be used in the chemical industry[171] as coatings, and as liquids in aeroplane hydraulic systems[170]. They can be used at temperatures up to 200°C [168] in fuel and lubricant systems, that is, where copolymers of butadiene and acrylonitrile are unsuitable[166]. 1F2 rubber, which has better frost resistance, can be used in the same branches of technology[172].

A large number of publications, mainly patent specifications, deal with the production of copolymers of 1,1-dihydroperfluoroalkyl acrylates with various vinyl monomers. To obtain copolymers with dienes, block copolymerisation is not very suitable since the polymerisation is complicated by a Diels–Alder condensation[173]. The latter can be avoided by carrying out the copolymerisation in emulsion and in the absence of oxygen. Copolymers with butadiene exhibit increased frost resistance[158,174] (glass point = −75°C), but tend to swell[167]. They are readily vulcanised by the agents listed above, and also by sulphur[151,165,169].

Methods of making copolymers of 1,1-dihydroperfluoroalkyl acrylates with ethyl acrylate[154,175], acrylamide[153], acrylonitrile[153,157], methacrylamide[152], ethylene[176], and trifluoroethyl vinyl ether[159]. The presence in the copolymer of fluorinated groupings confers noninflammibility on the polymer[177], and the joint presence of fluorine and chlorine allows the polymers also to be used as adhesives[178]. Copolymers with methacrylyl chloride are used for the chemical modification of wool[179] and copolymers with butadiene and acrylic acid have been proposed for use as regulators of the combustion of rocket fuel[180].

Elastomeric properties are also exhibited by copolymers of allyl esters of fluorine-containing acids[181]. Polyesters with branched fluorinated radicals[182] and also polyesters the alcohol residues of which contain ester[183], amide[184], or sulphamide[185] groups have been proposed for use for the protection of cloth or leather from the action of solvents, dyes, oil, etc.

Table 2. Properties of resins from polyesters 1F4 and 1F2.

Property	Resins from	
	1F4	1F2
Tensile strength, kgf cm^{-2}	84	70
Stress at 300% extension, kgf cm^{-2}	71	47
Relative elongation, %	360	400
Recoil elasticity	6	12
Frost resistance after Dzhimen, T_{10}, °C	−7	−30
Brittleness temp., °C	−13	−40
Swelling, %		
in benzene	17	15
in acetone	26	19
in 7 : 3 iso-octane : toluene mixture	91	64

Fluorine-containing polyacrylates or polymethacrylates exhibit good water-, oil-, and dirt-repelling properties[186]. The investigation of polymers with fluorinated radicals of various lengths showed that groupings in which the number of fluorinated carbon atoms is less than 5 do not give rise to an oil-repelling effect, whereas increasing the number of these atoms to 8 gives the polyesters superlative oil repellance[187]. On replacing even a single fluorine atom in the ω position by hydrogen, the oil repellence effect disappears completely and the surface tension rises sharply. Thus for polyacrylates with perfluoroalkyl substituents, in the composition of which there are eight carbon atoms[188], γ_S is ~11 dyn cm^{-1}, which is comparable with values of γ_S for perfluorohexan-1-oic acid (8.6 dyn cm^{-1}) and perfluoro-octan-1-oic acid (7.9 dyn cm^{-1}). In investigating copolymers of fluoroalkyl acrylates with non-fluorinated vinyl monomers γ_S increases in proportion to the number of the latter introduced[189]. If the second monomer contains fluorine atoms, then γ_S decreases. Evidently, lateral fluorinated substituents are orientated vertically (in relation to the polymer chain) and packed densely, like the packing in the molecular layers of perfluorocarboxylic acids. The capability for orientation and close packing in the surface layer depends on the length of the fluorinated parts of the chain and on the structure and dimensions of the side-chains as a whole.

The influence of the lateral fluorinated substituents on the formation of ordered (syndiotactic) structure was noted in the investigation of polymers, synthesised from esters of methacrylic acid and fluorinated monohydric alcohols[190]. Polymethacrylic acid obtained after the hydrolysis of such polyesters is found in syndiotactic form. The vinyl esters of fluorocarboxylic acids are readily polymerised by a radical mechanism, and the poly(vinyl alcohol) obtained as a result of hydrolysis contains ~80% syndiotactic diads[190-193].

The value of γ_S is somewhat increased on replacing a linear fluorinated radical by a branched one[194] in those instances when the latter is separated from the chain by several methylene groups but the oil-repelling properties of the polymer disappear[195]. When the branched radical is directly connected with acrylic acid, the γ_S is less[196]. Such polyesters have been suggested for use to give wool oil- and water-repelling properties[197].

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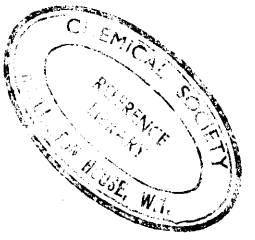

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The Anomeric Effect

N.S.Zefirov and N.M.Shekhtman

One of the problems of dynamic stereochemistry and conformational analysis—the anomeric effect—is surveyed, and is shown to be a general conformational phenomenon occurring widely in acyclic and heterocyclic compounds. A theoretical discussion is given of the nature of this effect. The bibliography comprises 189 references.

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I. INTRODUCTION

At the present time conformational analysis is based, in its most general form, on examination of the energy contributions made by changes in bond angles and lengths, by eclipsed conformations, and by interaction between non-bonded atoms. The energy of the molecule can be written as a sum

$$E_{mol} = E_l + E_p + E_Q + E_V,$$

where E_l is the sum of the energies due to change in bond lengths from the normal to the observed value, E_p the sum of "Pitzer stresses", E_Q the sum of the angular stresses, and E_V the sum of the van der Waals interaction energies of non-bonded atoms. An additive scheme involving all these steric factors enables the conformations of a wide range of compounds to be calculated fairly accurately[1-4].

Quite a large number of cases have now accumulated in the literature in which the stability of the conformations actually observed cannot be explained solely by steric factors. This type of discrepancy is usually regarded as specific to a given grouping, and is often given a special name, e.g. "anomeric effect"[5,6], "the rabbit's-ears effect"[7-10], the Δ^2 instability factor[5,11], etc. In principle these factors can be taken into account by introducing new terms into the expression for the energy of the molecule.

The present paper examines one such effect—the so called "anomeric" effect.

II. HISTORICAL SURVEY

The oxan ring is able to exist as conformational isomers differing in stability. In contrast to cyclohexane, the

asymmetry of the oxan ring increases the number of possible conformational isomers for derivatives of this series [12]: whereas two conformations (chair and boat [13-15]) are possible for cyclohexane, the oxan ring can exist as two chair conformations (1C and C1) and several boat conformations [16], e.g. (see Ref. 12 for greater detail)

As with cyclohexane the boat conformations are energetically less advantageous. Taking the barrier to rotation in methanol as 1.1 kcal mole^{-1} indicated that for oxan the energy of the boat form exceeded that of the chair form by 3.9 kcal mole^{-1}. [17] As a comparison, ΔH for the chair $\rightleftharpoons$ boat equilibrium in cyclohexane is 5.9 kcal mole^{-1}. [18] This estimate is undoubtedly too low, since it would be more logical to base it on the barrier to rotation in dimethyl ether [19], which is 2.7 kcal mole^{-1}. [20,21] This is confirmed by the estimate of 2.2 kcal mole^{-1} for the difference in energy between chair and boat conformations of 1,3-dioxan, based on the barrier to rotation in methanol, whereas experimental determination gives ΔG = 5.7 kcal mole^{-1}, ΔH = 7.1 kcal mole^{-1}, and ΔS = 4.8 e.u. [22-24]

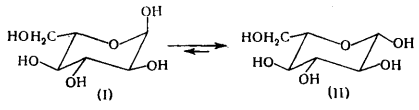
The barrier to chair $\rightleftharpoons$ boat conversion for oxan is 9.9 kcal mole^{-1}, [25,26] which is close to the value (10.3 kcal mole^{-1} [25]) found for cyclohexane.

The presence of chairlike conformations in a large number of pyranoses has been shown by X-ray examination [27-29], microwave spectroscopy [30], and nuclear magnetic resonance spectroscopy [25,26]. The R-factor which enables the departure from a chairlike conformation to be assessed, also has similar values—1.9 in oxan [31] and 2.2 in cyclohexane [32].

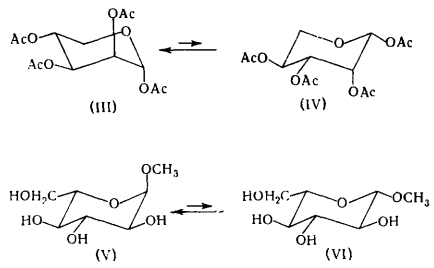
Thus the similarity in the geometry of oxan and cyclohexane enables us to apply general conformational rules to derivatives of the former compound.

The introduction by Reeves of conformational ideas into carbohydrate chemistry showed their complete applicability to this class of compounds, but also revealed the influence of specific "factors" on the relative stability of the conformations [16]. In particular we may mention e.g. the so called Δ^2 instability factor [11,16].

With free sugars both α- and β-forms are usually stable in solution (see Ref. 33 for a detailed scheme of the conformations of pyranoses). For the mutarotation of glucose in aqueous solution, for example, the equatorial form (II) has been shown to be the more stable, with ΔG_{OH} = 0.34 kcal mole^{-1}. [34,35] However, Lemieux [5] and other workers [36-39] have shown that several simple aglycones among pyranose derivatives tend in general to occupy the axial position. Lemieux termed this phenomenon the "anomeric effect" [6].



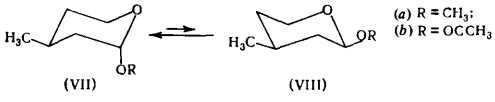
Detailed studies of the anomeric effect have been made on the $\alpha\beta$-anomerisation of pentose acetates [5], methyl pentosides [36,37,40-42], and halogeno- and acetoxy-derivatives of carbohydrates [38,43-46]. For example, 1,2,3,4-tetra-*O*-acetyl-α-D-lyxopyranose exists predominantly as the conformation (III), [5] whereas with methyl glucoside the α-anomer (V) is more stable than the β-anomer (VI). [42]



The first attempt to explain the anomeric effect was made by Edward [42], whose main idea was to examine the dipole–dipole interaction between the electronegative substituent and the ring oxygen atom. Such electrostatic interaction should be fairly large for an equatorial substituent, and slight for an axial substituent, in position 2.

Several quantitative estimates have been made of the anomeric effect in derivatives of monosaccharides. For example, Bishop [40] found a value of ~ 1.2 kcal mole^{-1} for the anomerisation of methyl pentosides in methanol. The most complete estimates of the anomerisation of sugars were given by Lemieux [5], with 1.5 and 1.3 kcal mole^{-1} respectively for the anomeric effect of the acetoxy-group in hexoses and in pentapyranoses. On the bases of these results he proposed a convenient additive scheme for calculating the preferential conformations of derivatives of monosaccharides.

In 1964 Anderson and Sepp found that the equilibrium mixtures of 2-methoxy- and 2-acetoxy-4-methyloxans contain 65% and 70% respectively of the axial forms of the compounds (VII*a*) and (VII*b*), [47] and thus showed that the anomeric effect should be a general phenomenon.



The impossibility of allowing for all the factors—all the dipole–dipole interactions, solvation, hydrogen bonds, deviations in the conformations from the standard chair forms in polysubstituted compounds, etc.—also makes it difficult to study the anomeric effect on models of monosaccharides. During recent years, therefore, various aspects of the anomeric effect have been studied extremely intensively on simple models. The investigations have shown without question that the anomeric effect is a general conformational phenomenon, unconnected with the specific structure of sugars and extremely widespread among heterocyclic compounds.

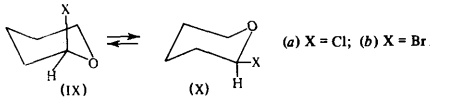
The literature on the anomeric effect has grown very rapidly since 1965. Several reviews have been published during recent years [5,33,48-50], but they are very concise and do not contain the full results. It therefore appeared to us useful to summarise in a special review the existing literature on the anomeric effect. It is systematically based on differences in the structural fragments comprising the cyclic heteroatom and the substituent atom directly attached to the ring.

III. THE ANOMERIC EFFECT IN SIX-MEMBERED CYCLIC STRUCTURES

1. The O–C–Hal Fragment

(*a*) Halogenated oxans

The conformational equilibrium of 2-halogeno-oxans can be represented by the equation



(*a*) X = Cl; (*b*) X = Br

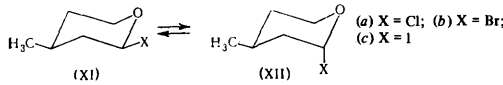
The conformational free energy of chlorine and bromine in the cyclohexane series is 0.43 [51] (0.53 [52]) and 0.38 [51] (0.48 [52]) kcal mole^{-1} in favour of predominance of the equatorial form.

Nuclear magnetic resonance has been used by Booth and Ouellette [53] and by Zefirov and Shekhtman [54,55] to study the conformational equilibrium of 2-chloro- and 2-bromo-oxans. They showed that the proportion of the equatorial form is very small in both compounds, the equilibrium being displaced almost completely towards the axial isomer (IX). The free energy of the conformational equilibrium (IX) $\rightleftharpoons$ (X) was estimated as 1.8 kcal mole^{-1}. The magnitude of the anomeric effect can be written

$$\Delta G_{AH} = \Delta G_0 - \Delta G_x,$$

where ΔG_0 is the equilibrium free energy and ΔG_X the conformational free energy of the substituent in the cyclohexane series [47] (this view has been criticised [56]). In this case the anomeric effect is estimated as 2.3 kcal mole^{-1}. Variation in the polarity of the solvent has very little influence on the position of the conformational equilibrium (IX) $\rightleftharpoons$ (X). [53] It is interesting that the n.m.r. spectrum of (IX*a*) shows a reversal of the chemical shifts of the signals from the axial and the equatorial proton attached to $C_{(6)}$. [55]

The above results [53–55] were based on a semi-quantitative estimate of the equilibrium position from the spin–spin interaction constants. A more exact estimate of the anomeric effect was made by Anderson and Sepp [57] in a study of the epimerisation of 2-halogeno-4-methyloxans (XI) and (XII) (*a*–*c*)

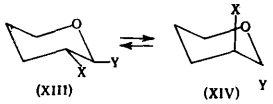


(*a*) X = Cl; (*b*) X = Br; (*c*) X = I

From data on the epimerisation equilibrium the anomeric effect for chlorine was estimated as 2.65 and 2.0 kcal mole^{-1} for non-polar and polar solvents respectively. The anomeric effect for bromine and iodine was ~ 3.1 kcal mole^{-1}.

Gas chromatography showed that 2-chloro-oxan comprises a mixture of equal quantities of axial and equatorial forms (IX*a*) and (X*a*). [58] However, this conclusion is undoubtedly erroneous, since it contradicts all the work cited above. Furthermore, the preferred axial conformation of this compound has recently been proved by measuring the Kerr constants and the dipole moments [59].

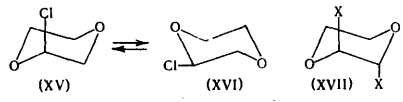
Lemieux and Fraser-Reid [43] found that *trans*-2,3-dichloro- and bromo-oxans exist predominantly as the *trans*-diaxial conformation (XIV).



In this case the position of the conformational equilibrium is determined not only by the anomeric effect but probably also by 1,2-repulsion of the halogen atoms in the diequatorial conformation. This effect has been studied in some detail among cyclohexane derivatives [60–62].

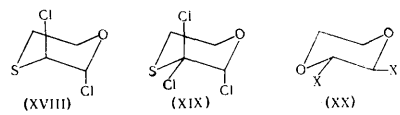
(*b*) Halogenated dioxans and oxathians

Zefirov and Fedorovskaya [63] observed a distinct anomeric effect with 2-chloro-1,4-dioxan. The equilibrium (XV) $\rightleftharpoons$ (XVI) was extensively displaced towards the axial isomer (XV), the position of the conformational equilibrium being as little affected by the polarity of the solvent as in the case of 2-halogeno-oxans.

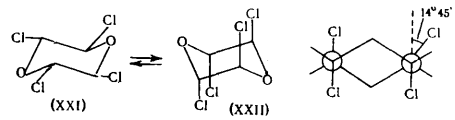


(X = Cl, Br)

Much work has been done on elucidating the configurations and preferred conformations of 2,3-dihalogeno-1,4-dioxans [64–68]. X-Ray examination has shown that the *trans*-isomers of 2,3-dichloro- and 2,3-dibromo-1,4-dioxans exist in the diaxial conformation (XVII). [64,65] Nuclear magnetic resonance has shown that in solution *trans*-2,3-dichloro-, -2,3-dibromo-, and -2,5-dichloro-1,4-dioxans also occur in the diaxial conformation [64,65,67–70]. Wolf and his coworkers [71,72] have studied the conformations of many polychlorinated oxathians and established a distinct anomeric effect in the halogenated derivatives. For example, *trans*-2,3-dichloro-oxathian and 2,3,3-trichloro-oxathian have the more stable conformations (XVIII) and (XIX) respectively.



It is probable that, as with 2,3-dichloro-oxan, the axial conformations of 2,3-dihalogenodioxans and 2,3-dichloro-oxathian are due not only to an anomeric effect but also to repulsion of the halogen atoms in the diequatorial conformation (XX).

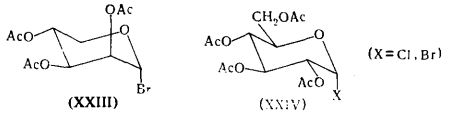


Extraordinarily interesting results have been obtained in a study of the crystalline structure of *trans*-2,3,5,6-tetrachloro-1,4-dioxan [73]. In spite of strong 1,3-interactions, the stable conformation is (XXII), in which all four chlorine atoms are axial. The C–Cl bond is inclined at an angle of 14°45′ to the vertical position.

(*c*) Pyranosyl halides

Numerous examples of pyranosyl halides have shown that the form in which the halogen is in an axial position is usually the more stable [5,11,38,39,45,74]. Thus (XXIII) and

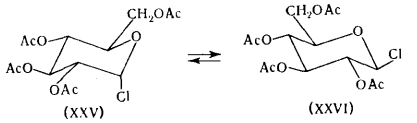
(XXIV) are the stable conformations of tri-*O*-acetyl-D-lyxopyranosyl bromide and tetra-*O*-acetyl-α-D-glucopyranosyl halides respectively.



(XXIII) (XXIV)

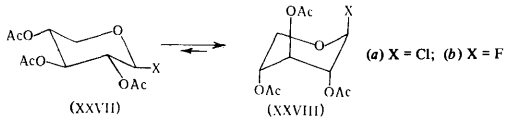
The anomerisation of pyranosyl halides should occur extremely readily, since the halogen atom is capable of nucleophilic detachment and the cyclic oxygen atom greatly stabilises the resulting carbonium ion. Since anomerisation occurs smoothly, therefore, the main factor determining the relative stability of the epimers is the anomeric effect.

Lemieux and Hayami [75] estimated the anomeric effect of the chlorine atom attached to $C_{(1)}$ in acetochloroglucose as ~ 2 kcal mole^{-1} in acetonitrile (taking into account ΔG_{Cl}), which corresponds to the presence of 93–95% of the α-anomer (XXV) in the equilibrium mixture.



(XXV) (XXVI)

In several cases the anomeric effect is sufficiently large to displace the equilibrium to a "completely" axial conformation. Very interesting examples of this type are provided by β-D-xylopyranosyl chloride and fluoride, the most stable conformations of which are (XXVIII*a*) and (XXVIII*b*), in which all four constituents are in axial positions [33,76–79]:

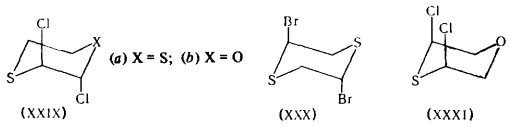


(XXVII) (XXVIII)

The 1,3-diaxial repulsion of two acetoxy-groups in the cyclohexane series has been estimated as 2.0 kcal mole^{-1}. [80] Although the structure (XXVIII) involves two 1,3-diaxial repulsions, this conformation is the more stable.

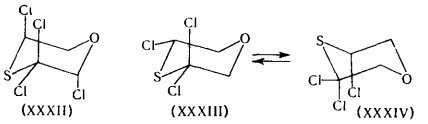
2. The S–C–Hal Fragment

The repulsion between sulphur and halogen atoms is sufficient to destabilise the equatorial conformation. Kalff and Romers [81,82] made an X-ray examination of *trans*-2,3-dichlorodithian and *trans*-2,5-dibromodithian, and found them to have the conformations (XXIX*a*) and (XXX) respectively.



(XXIX) (XXX) (XXXI)

Few data are available on the conformations of compounds of this type in solution. Study of the infrared spectra and dipole moments of *trans*-2,3-dichloro- and *trans*-2,5-dibromo-1,4-dithians has shown [72] that these compounds have the same conformations as in the crystal. It has been found [71,72,83] that *trans*-2,3-dichloro-, *cis*-3,5-dichloro-, *trans*-2,3,3,5-tetrachloro-, and 3,3,5-trichloro-oxathians have the preferred conformations (XXIX*b*) and (XXXI)–(XXXIII) respectively.



(XXXII) (XXXIII) (XXXIV)

These results are based on the vicinal spin–spin splitting constants. When compounds (XXXI)–(XXXIII) are compared, however, it remains obscure why the diaxial repulsion of the halogen atoms destabilises the conformation (XXIV), although this does not occur with compound (XXXI). It is also noteworthy that in several cases the quantity J_{ee} was of the order of 6–8 c/s, which perhaps indicates the presence of a mobile equilibrium, e.g. (XXXIII) ⇌ (XXXIV).

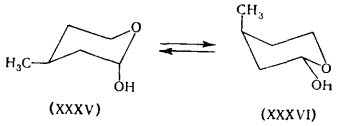
3. The O–C–OR Fragment

(*a*) Hydroxy-derivatives (R = H)

Oxan-2-ol is a cyclic tautomer of hydroxyvaleraldehyde, and according to the infrared spectra [84] exists in the hemiacetal form. It is well known that cyclic hemiacetal forms predominate with monosaccharides. It has already been remarked that the polarity of the solvent has relatively little effect on the position of the conformational equilibrium in 2-halogenated oxans, but the situation is quite different with the 2-hydroxylated derivatives.

The position of the conformational equilibrium is considerably changed by transfer from aprotic solvents to water, being displaced towards the equatorial form. This applies also to cyclohexanols, for which the mean values of ΔG_{OH} are 0.54 and 0.87 kcal mole^{-1} in aprotic solvents and in water respectively [51]. Stabilisation of the equatorial conformation of 2-hydroxylated oxans in water may be due either to an increase in the dielectric constant of the medium, which diminishes the anomeric effect, or to strong solvation of the hydroxy-group, which increases its effective volume.

In fact, Anderson and Sepp [85] found that the transfer from aprotic solvents to water produces a marked change in the conformational equilibrium for *trans*-4-methyloxan-2-ol: in water this compound exists to the extent of 66% in the equatorial conformation, whereas in carbon tetrachloride the conformation (XXV) with an axial hydroxyl predominates (60%):



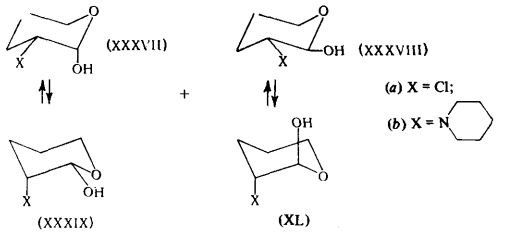
(XXXV) (XXXVI)

Pierson and Runquist showed by means of n.m.r. spectroscopy that the proportion of the axial isomer in oxan-2-ol is 77% in non-polar solvents [86]. This result is confirmed by infrared spectroscopy. Thus in 5% solution in carbon tetrachloride, for example, the conformation having an axial hydroxyl predominates, its proportion increasing further with dilution [85].

It is interesting that a distinct anomeric effect has been observed [87] with chroman-2-ol both in acetonitrile and in carbon tetrachloride, the proportion of the axial isomer (80–85%) being independent of the concentration.

The equilibrium mixture of oxan-2,3-diol in deuterochloroform has been shown by the n.m.r. spectra to comprise 30% of *cis*- and 70% of *trans*-diequatorial isomers[88]. The decisive part in stabilisation is probably played by an intramolecular hydrogen bond[89].

In dimethyl sulphoxide the addition product of hypochlorous acid and dihydropyran comprises a mixture of *cis*- and *trans*-isomers in the proportions 37 : 63, with $J_{2,3} = 5.6$ c/s for the *trans*-isomer, which suggests the presence in conformational equilibrium (XXXVIII) ⇌ (XL*a*) of an appreciable fraction of the diaxial form (XL*a*).[90]



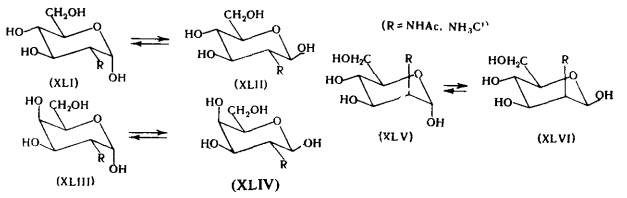
The equilibrium mixture of 3-piperidino-oxan-2-ol comprises 46% of the *cis*-isomer (XXXVII) ⇌ (XXXIX*b*) and 54% of the *trans*-isomer (XXXVIII*b*) ⇌ (XL*b*). For the *trans*-isomer $J_{2,3} = 6.6$ c/s,[91] which also indicates predominance of the diequatorial conformation (XXXVIII*b*).

Thus with oxan-2-ol derivatives in protic solvents the conformation in which the hydroxyl is in an equatorial position is usually the more stable.

The conformation of sugars and their $\alpha\beta$-anomerisation are well known[5,33,40,48,74,92,93], and we shall not discuss this subject in detail. We note merely that the magnitude of the anomeric effect in monosaccharides may be affected by a far larger number of factors than in the case of oxan-2-ol. As with the latter, the anomeric effect is influenced primarily by the nature of the solvent. Thus the equilibrium mixture of glucose in absolute methanol contains equal quantities of α- and β-forms, which gives an anomeric effect of 0.9 kcal mole^{-1},[94] but in water the proportions of the two forms are 36 : 64.[48,95] In a pyridine solution of mannose the equilibrium mixture contains 85% of the α-form[96] (the calculated anomeric effect is 1.15 kcal mole^{-1} [94]). The magnitude of the effect increases in non-polar solvents[94].

It has been found with aldopyranoses that the configuration of the hydroxyl attached to the $C_{(2)}$ atom greatly influences the magnitude of the anomeric effect[48]. Angyal showed that, in the absence of a 2-hydroxyl, the effect in pyranoses is 0.85 kcal mole^{-1}; if the hydroxyl is axial the effect is 1.0 kcal mole^{-1} (except when the 3-hydroxyl is also axial); and finally the anomeric effect is 0.55 kcal mole^{-1} when the 2-hydroxyl is equatorial (all values of the anomeric effect were calculated with ΔG_{OH} taken into account).

Polarimetric data and n.m.r. spectra have shown that replacement of the 2-hydroxyl in a series of D-gluco- and D-galacto-pyranoses by an acetamido-group or by an ammonium group results in greater stability of the α-forms (XLI) and (XLIII), whereas with D-mannose the β-form (XLVI) is stabilised[97,98].



Thus a great variety of factors—solvent, intramolecular hydrogen bonds, specific solvation, nature of substituent adjacent to anomeric centre, etc.—influence the conformational equilibrium of oxanols.

(*b*) Alkoxyoxans

Alkoxyoxans are very convenient models for examining various factors influencing the anomeric effect, as a consequence of which they are probably the most thoroughly studied. Zefirov and Shekhtman[54,55] and Pierson and Runquist[86] have made semi-quantitative assessments of the position of the conformational equilibrium and the magnitude of the anomeric effect for a wide range of 2-substituted oxans. These workers have found that 2-alkoxyoxans do exhibit an anomeric effect, whose value varies somewhat with the polarity of the solvent. Thus the anomeric effect for a series of 2-alkoxyoxans varies over the range 1.3–2.8 kcal mole^{-1} in non-polar solvents, and over the range 1.25–1.9 kcal mole^{-1} in acetonitrile[49,54,55].

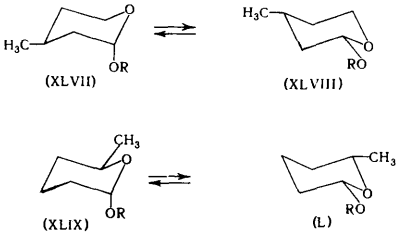
The electronegativity of the substituent undoubtedly affects the position of conformational equilibrium. There is probably a general tendency for the anomeric effect to increase slightly with electronegativity. Quantitative correlation is difficult, however, because of the lack of reliable and accurate data on the position of conformational equilibrium for a wide range of substituents. Pierson and Runquist[86] tried to correlate the free energy for the equilibrium in a series of 2-alkoxyoxans with the Taft inductive σ^*-constants for the radical in the alkoxy-group. However, the resulting correlation can hardly be regarded as in any way reliable owing to the crudity with which the equilibrium position was estimated.

The position of conformational equilibrium in 2-alkoxyoxans appears to be relatively insensitive to the size of the radical in the alkoxy-group[7,54,55,86,99].

It is interesting that α-fenchol reacts with dihydropyran to yield two compounds, which have been regarded as conformational isomers containing an axial and an equatorial fenchyloxy-group[100]. Such separation of conformers is obviously unprecedented, and it is probable that these workers were actually dealing with structural isomers.

The nature of the solvent has a relatively weak influence on the anomeric effect, although a certain tendency is observed for the content of the axial form to increase with decrease in the polarity of the medium[7,47,54,85,86,101].

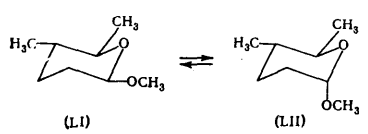
More exact data were obtained by Anderson and Sepp[57,101] and also by Eliel and Giza[56] in a study of the epimerisation of 2-alkoxy-4-methylpyrans (XLVII) ⇌ (XLVIII) and 2-alkoxy-6-methylpyrans (XLIX) ⇌ (L). They found a distinct dependence of the anomeric effect on the solvent. Thus ΔG for 2-methoxy-4-(and 6)-methyloxans in carbon tetrachloride is respectively 0.83 and 0.73 kcal mole^{-1} (corresponding to 80% and 67% of the anomer XLVII), whereas in acetonitrile the values are 0.42 and 0.35 kcal mole^{-1} (67% and 64% of the anomer XLVII).[56,102]



The size of the alkoxy-group has been considered[85] to have no significant influence on the position of the conformational equilibrium. In fact, the proportion of the *trans*-form (XLVII) remains almost unchanged on passing from the methoxy- to the isobutoxy-group. Thus in acetonitrile, for example, 65% of (XLVII) is present in the case of 2-methoxy-4-methyloxan, and 70% with 2-isobutoxy-4-methyloxan. Other workers[56], however, have noted a definite and monotonic decrease in the proportion of axial conformations (XLVII) and (XLIX) with increase in the bulk of the radical in the alkoxy-group. Thus $\Delta G(CCl_4)$ has the values 0.73, 0.64, and 0.5 kcal mole^{-1} for the methoxy-, isopropoxy-, and t-butoxy-groups in the 2-alkoxy-6-methyloxans.

The position of the conformational equilibrium in alkylated 2-alkoxyoxans is relatively insensitive to the location of the alkyl substituent in the ring[56,85,101]. Thus 2-methoxy-4-methyloxan in methanol contains 69% [101] (67.3% [56]) of the conformation (XLVII), while in 2-methoxy-6-methyloxan the content of the axial isomer (XLIX) under the same conditions is 70% [101] (62.5% [56]).

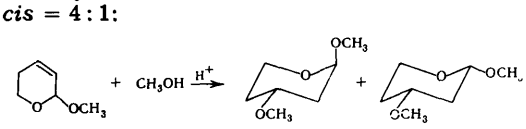
It has been pointed out[101] that the proportion of the axial form is greater with methyl glucoside than with methyl xyloside and 2-methoxyoxan. The explanation offered was that the presence of two bulky groups in positions $C_{(5)}$ and $C_{(6)}$ of the oxan ring in the equatorial position results in their steric repulsion, which may lead to a slight flattening of the ring and hence an increase in the distance between the axial 6- and 2-substituents, so that the steric repulsion of the 2-substituents is diminished. This effect has been confirmed experimentally on the isomeric 2-methoxy-5,6-dimethyloxans[101]. It was observed that the epimerisation of 2-methoxy-*trans*-5,6-dimethyloxans yields an equilibrium mixture in which the content of the isomer (LII) reaches 77%.



(LI) (LII)

Distinct anomeric effects have been observed also with oxanyloxy-,[103] trimethylsiloxy-,[54] t-butylperoxy-,[104] and alkylthio-oxans[103].

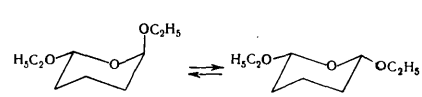
Sweet and Brown[105] showed that the addition of methanol to 5,6-dihydro-2-methoxy-2*H*-pyran yields a mixture of 2,4-dimethoxyoxans in which the ratio of the isomers is *trans* : *cis* = 4 : 1:



(LIII) (LIV)

Since the reaction was conducted in acid medium, the composition of the mixture was probably controlled thermodynamically. The n.m.r. spectra showed that the 4-methoxy-group occupied an equatorial position, while the anomeric effect in methanol was 1.4 kcal mole^{-1}. The difference in magnitude of the anomeric effect in (LIII) and (XLVII)—that of the latter compound in methanol is[85] 0.9 kcal mole^{-1}—was regarded[105] as a good illustration of the polar nature of the anomeric effect.

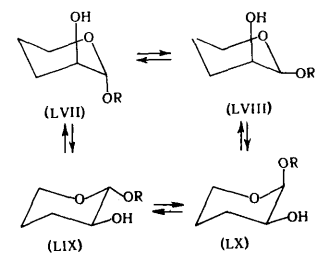
The anomeric effects of 2,6-diethoxyoxans



(LV) (LVI)

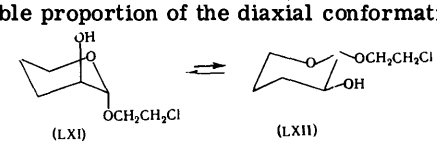
and of 2-ethoxy-4(or 6)-methyloxans are almost the same[56,108] when it is remembered that the *trans*-isomer (LV) is a DL-pair, so that ΔG is increased by $RT\ln 2 = 0.41$ kcal mole^{-1}. It is found also that with increase in the polarity of the solvent the equilibrium (LV) $\rightleftharpoons$ (LVI) is displaced towards the *cis*-isomer. Thus ΔG for this equilibrium has the values 1.16, 0.76, and 0.89 kcal mole^{-1} in carbon tetrachloride, acetonitrile, and ethanol respectively[56].

There is no published information on the conformations of 2,3-dialkoxyoxans, but 2-alkoxyoxan-3-ols have been studied by several workers. Although the n.m.r. data[107,108] are somewhat contradictory, there is no doubt about the predominance of the *trans*-diaxial form (LVII) and the presence of an anomeric effect; the size of the alkoxy-group has hardly any influence on the position of the conformational equilibrium[108].



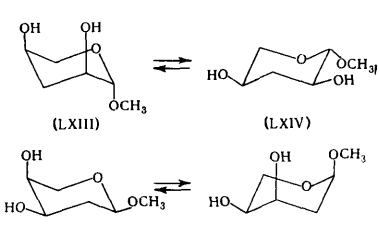
(LVII) (LVIII) (LIX) (LX)

The *trans*-isomer of 2-2′-chloroethoxyoxan-3-ol has $J_{3,2} = 5$ c/s in deuterochloroform[88], which also suggests a considerable proportion of the diaxial conformation (LXI).



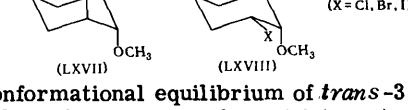
(LXI) (LXII)

Lemieux and Pavia[109] found that the nature of the solvent was the main factor determining the conformations of methyl 3-deoxy-β-L-erythropentapyranoside and 2-deoxy-L-erythropentapyranoside. In deuterium oxide the compounds exist in the conformations (LXIV) and (LXV), but in deuterochloroform as (LXIII) and (LXVI) respectively. The n.m.r. data correlate well with the specific rotations.



(LXIII) (LXIV) (LXV) (LXVI)

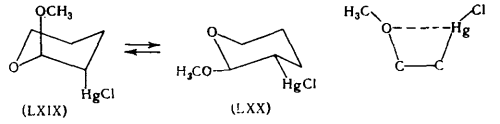
The halogenomethoxylation of dihydropyran yields a mixture of 3-halogeno-2-methoxyoxans. The *trans*-isomer exists in the diaxial conformation (LXVII), and the *cis*-isomer in the equatorial–axial conformation (LXVIII).[43] Iodomethoxylation results in the formation of 100% of (LXVII), whereas chloromethoxylation gives 75% of (LXVII) and 25% of LXVIII).



(LXVII) (LXVIII) (X = Cl, Br, I)

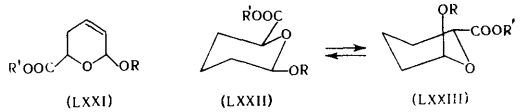
The conformational equilibrium of *trans*-3-chloromercuri-2-methoxyoxan is of great interest. Since $\Delta G_{HgCl} \simeq 0$ (the value of ΔG for the $HgOCOCH_3$ group is[52]

0 ± 0.09 kcal mole^{-1}), and also because of the anomeric effect of the methoxy-group, the conformation (LXIX) should predominate. According to Zefirov and Shekhtman[55], however, the diequatorial conformation (LXX) is stable. This was explained by the additional effect of coordination of the methoxyl oxygen and the mercury atom, which stabilises (LXX). The magnitude of this effect is 0.95 kcal mole^{-1} with ΔG^{OCH_3} taken into account.



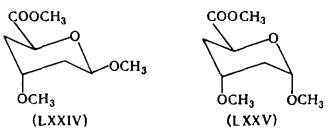
(LXIX) (LXX)

The n.m.r. spectra of Δ^3-dihydropyrans (LXXI) (obtained by Diels–Alder condensation of 1-alkoxyalka-1,3-dienes with carbonyl-containing compounds) and of the corresponding oxans indicate that isomers having shorter retention times in gas–liquid chromatography comprise more than 90% *trans-ax,eq*-isomers with the alkoxy-group in the axial position, whereas isomers having longer retention times comprise not less than 90% of *cis-eq,eq*-isomers[110,111]. Epimerisation in the presence of boron trifluoride leads to the conversion of *cis*-isomers (LXXII) into *trans*-isomers (LXXIII).



(LXXI) (LXXII) (LXXIII)

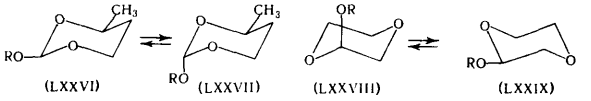
It is interesting that, in the case of methyl 4,6-dimethoxyoxan-2-carboxylate, the *ribo*-configuration (LXXV) is more stable than the *arabino*-isomer (LXXIV), in spite of the 1,3-diaxial arrangement of the methoxy-groups[112].



(LXXIV) (LXXV)

(*c*) Alkoxy-derivatives of saturated six-membered heterocycles containing two heteroatoms

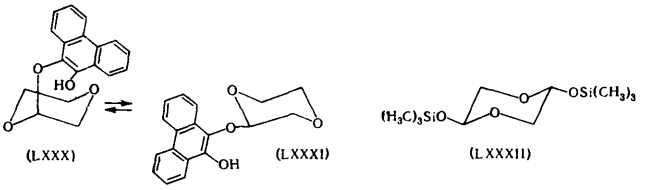
Eliel and Giza[10,56] observed a distinct anomeric effect with 2-alkoxy-1,3-dioxans. The epimerisation of 2-methoxy(and ethoxy)-4-methyl-1,3-dioxans (LXXVI) ⇌ (LXXVII) results in predominance of the *cis*-isomer (LXXVII), with $\Delta G^{OR} = 0.35$ kcal mole^{-1} in carbon tetrachloride. For 2-methyl-1,3-dioxan $\Delta G^{CH_3} = 3.6-4.1$ kcal mole^{-1}, which far exceeds the value of 1.7 kcal mole^{-1} observed for methylcyclohexane[51].



(LXXVI) (LXXVII) (LXXVIII) (LXXIX)

Zefirov and Fedorovskaya used the n.m.r. method to show that the anomeric effect applies to 2-alkoxy-1,4-dioxans[63,113]. In contrast to 2-alkoxyoxans[7,54,55,86,99], however, their conformational equilibrium (LXXVIII) ⇌ (LXXIX) is more sensitive to the volume of the substituent in the alkoxyl. Thus the (LXXIX) content increases by about 25% on passing from the methoxy- to the t-butoxy-group at position 2.[63]

Similar results have been obtained for 2-phenanthryloxy-1,4-dioxan, in which the steric effect predominantes over the polar effect, so that the conformational equilibrium is displaced towards the equatorial isomer (LXXXI):[114]



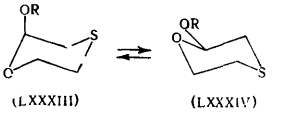
(LXXX) (LXXXI) (LXXXII)

A general explanation of this phenomenon can be given in terms of the "hockey-stick effect" (see below).

It is interesting that in the n.m.r. spectrum of 2,5-bis-trimethylsiloxy-1,4-dioxan $J_{AX} = 6.0$ c/s and $J_{BX} = 2.4$ c/s (in carbon tetrachloride), so that a diequatorial conformation (LXXXII) was adopted for this compound[115]. For 2-t-butoxydioxan $J_{AX} + J_{BX} = 8.4$ c/s,[62] and in both cases the content of the diaxial conformation is ~ 45%.

Another pecularity of alkoxy-1,4-dioxans is that the effect of the solvent on the position of conformational equilibrium is opposite to that observed with oxan derivatives[7,47,54,85,86,101]. With 2-alkoxy-1,4-dioxans the proportion of the axial conformation increases somewhat on passing from carbon tetrachloride to acetonitrile, which may be due to fine solvation effects at the 4-oxygen atom[63].

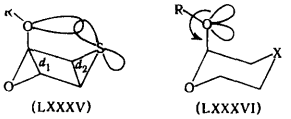
As already noted, introduction of the second heteroatom on passing from 2-alkoxyoxans to 2-alkoxydioxans has no great qualitative effect on the conformational behaviour. However, the situation changes radically on passing to 2-alkoxyoxathians, as Foster et al.[116] and Zefirov et al.[113,117] have shown. Thus with 2-methoxy- and 2-butoxy-oxathians at least 50% of the equatorial conformation (LXXXIV) is present at equilibrium.



(LXXXIII) (LXXXIV)

A strict interpretation of this phenomenon is difficult because of the absence of experimental conformational analyses of other, analogous heterocyclic systems. However, it is obvious that destabilisation of the axial conformation cannot be explained simply by dipole–dipole repulsion of the 4-heteroatom and the substituent, for such repulsion should be more strongly developed in 1,4-dioxan than in 1,4-oxathian derivatives.

A general explanation of this phenomenon can evidently be based on the "hockey-stick effect"[118]. For the R–O–C–C–S fragment, in particular, the orbital of the oxygen atom (p or sp^3) may overlap an orbital of the sulphur atom (p- or sp^3-hybrid), as shown in formula (LXXXV). Since these orbitals are populated by four electrons, such overlap should lead to repulsion. Such repulsion will evidently depend on the geometry of the molecule, in particular on the relative distances d_1 and d_2, and also on the nature of the atoms having lone pairs of electrons. Experimental results must be accumulated for a more detailed study of this phenomenon.



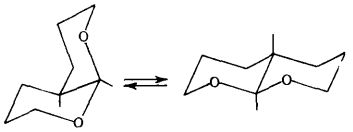
(LXXXV) (LXXXVI)

However, the "hockey-stick effect" enables an acceptable explanation to be given for the greater sensitivity noted above of the conformational equilibrium to the volume of the alkoxy-substituent in the 1,4-dioxan series than in

alkoxyoxans. In fact the most stable rotational conformation of the axial alkoxy-group is (LXXXVI), in which the radical R is directed outside the ring, and hence the orbitals of the oxygen atom containing lone pairs are directed inside the ring. Hence arises the possibility of repulsion of the 4-oxygen atom and the alkoxyl oxygen as a consequence of the "hockey-stick effect". If, however, the size of R is small, the group OR may adopt a more favourable rotational conformation, which will diminish such repulsion. When R is a bulky group, e.g. t-butyl, the mobility of OR is restricted significantly, and the orientation of OR observed with respect to $O_{(4)}$ leads to repulsion, which partly destabilises the axial conformation (LXXXVI).

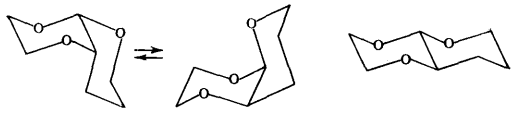
(*d*) Fused saturated systems

The axial forms of 3-alkoxy-4-oxa-5α-cholestanes and 3-methoxy-4-oxa-5α-oestranes are the more stable[119,120]. Thus an anomeric effect is clearly evident for the group O–C–O–C, which is a fragment of the polyfunctional fused systems.



(LXXXVII) (LXXXVIII)

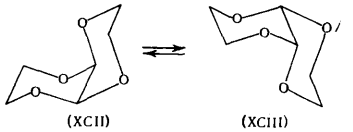
Descotes et al.[121] have shown by the n.m.r. method that the epimerisation of decahydro-1,8-dioxanaphthalene yields an equilibrium mixture of 57% of the *cis*-form (LXXXVII) and 43% of the *trans*-form (LXXXVIII), which differs markedly from the behaviour of decalin[122]. The relative stabilisation of the *cis*-isomer is explained by the anomeric effect, since the fragment O–C–O–C in this compound is analogous in (LXXXVII) to the O–C–O–R observed for the axial conformation of 2-alkoxyoxan, and the anomeric effect is of the same order in this case (1.4 kcal mole^{-1} [121]) as for simple 2-alkoxyoxans[84,101].



(LXXXIX) (XC) (XCI)

cis-Decahydro-1,4,5-trioxanaphthalene (LXXXIX) $\rightleftharpoons$ (XC) and the *trans*-isomer (XCI) were prepared by Sweet and Brown[88], and their structures proved by means of the n.m.r. spectra. Unfortunately these workers did not study the acid epimerisation, but it can be confidently stated that here the *cis*-isomer (XC) should be the more stable, as a consequence of the anomeric effect.

A *trans*-configuration was originally attributed to decahydro-1,4,5,8-tetraoxanaphthalene on the bais of X-ray data on its complex with mercurous chloride[123]. However, low-temperature n.m.r. spectroscopy has shown that this possesses a *cis*-configuration; the latter is more stable owing to the anomeric effect. The compound exists as two rapidly interconvertible conformations



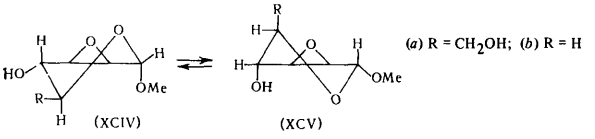
(XCII) (XCIII)

with $\Delta G^{\neq} = -11.5$ kcal mole^{-1}. [124–126]

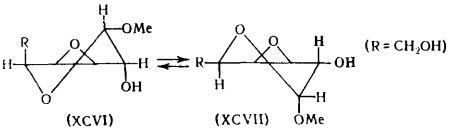
(*e*) Alkyl pyranosides

We have already mentioned in the Introduction that many examples have been shown of the preferential axial orientation of polar aglycones in the sugar series[36,37,40–42,67]. Lemieux[5] observed equilibrium proportions of 3 : 1 of α- and β-anomers in methyl 2,3,4,6-tetra-O-methyl-α- and -β-glucopyranosides in methanolic solution. Intramolecular rearrangement of methyl β-D-glucopyranoside triacetate catalysed by boron trifluoride and titanium tetrachloride gave a 90% yield of the α-anomer with an axial methoxy-group[127].

Methyl pyranosides contain approximately the same content (70%) of the axial isomer in conformational equilibrium[101] and exhibit a similar anomeric effect (1.2 kcal mole^{-1})[40] as the analogous 2-alkoxyoxans. The presence of many functional groups in alkyl pyranosides has enabled a broad study to be made of the various factors influencing the position of conformational equilibrium. Since most of the results of the large amount of work done on this problem can be found in review papers[5,33,48,50,101,128], we will not discuss it at length. We remark merely that an anomeric effect has been found also in polyacetylenic alcohols of glucosides[129].



(XCIV) (XCV) (*a*) R = CH_2OH; (*b*) R = H



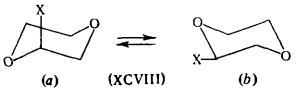
(XCVI) (XCVII) (R = CH_2OH)

In several cases the anomeric effect makes conformations having an axial alkoxy-group stable with 2,3- and 3,4-anhydroglucopyranosides[130–134]. In the case of the conformational equilibrium of methyl 2,3-anhydro-α-D-manno- and -lyxo-pyranosides, for example, the latter being especially interesting, (XCIV*a*) and (XCIV*b*) respectively are the stable conformations, but with methyl 3,4-anhydro-α-D-galactopyranoside the conformation (XCVII) is stable.

(*f*) Acetoxy-derivatives

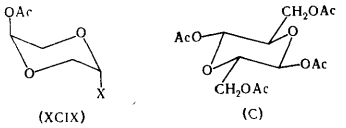
Anderson and Sepp[47,57,85] and Zefirov and Shekhtman[54] have shown that oxan-2-yl acetate and its alkyl derivatives have almost the same anomeric effect and similar contents (85–90%) of the axial form. The proportion of the axial isomer in the equilibrium mixture diminishes with increase in the polarity of the solvent.

The difference in electronegativity between the acetoxy- and the methoxy-group has a stronger influence on the position of conformational equilibrium in 2-alkoxy-1,4-dioxans. According to Zefirov and Fedorovskaya[63] the compound (XCVIII) in carbon tetrachloride consists of 68% of (XCVIII*a*) if X = OCH_3, and 95% if X = $OCOCH_3$.



(*a*) (XCVIII) (*b*)

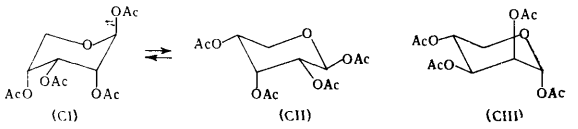
According to n.m.r. data 1,4-dioxan-2,5-diyl *trans*-diacetate consists almost entirely of the diaxial conformation (XCIX: X = $OCOCH_3$).[135] Nevertheless, the tetraequatorial conformation (C) of *trans*-2,5-diacetoxy-3,6-bisacetoxymethyl-1,4-dioxan is stable[135].



(XCIX) (C)

From results for the anomerisation and conformational equilibrium of pyranose acetates Lemieux[5] calculated the anomeric effects for hexoses and pentoses as 1.5 and 1.3 kcal mole^{-1} respectively. The difference between these values is probably due to the electronegativity of the 5-substituents and in particular the inductive effect of the 6-oxygen atom.

The increased content (88%) of the axial isomer in glucose penta-acetate in comparison with xylose tetra-acetate (78.5%) and oxan-2-yl acetate (75%) is attributed by Anderson and Sepp[101] not only to the polar effect of the 6-hydroxymethyl group but also to interaction of the 3- and 4-acetoxy-groups.

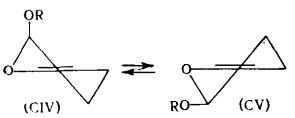


(CI) (CII) (CIII)

The conformational equilibrium of β-D-ribopyranose tetra-acetate (CI) ⇌ (CII) is displaced towards the *trans*-axial conformation (CII) by an anomeric effect[136]. α-D-Lyxopyranose tetra-acetate exists to the extent of 98% as the conformation (CIII).[138]

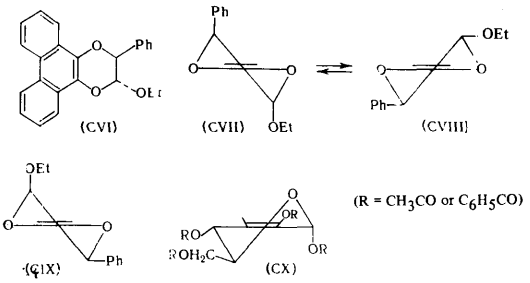
(*g*) Alkoxy-derivatives of dihydropyrans and dihydrobenzopyrans

The half chair is the preferred conformation of unsaturated and fused pyran derivatives containing a 5–6 double bond. Since ΔG_R decreases on passing from derivatives of cyclohexane to those of cyclohexene[137], a distinct anomeric effect was to be expected in dihydropyran derivatives. In fact Zefirov and Shekhtman found[54,87] with 2-alkoxy-3,4-dihydropyrans that the axial conformation (CIV) is predominant.



(CIV) (CV)

An anomeric effect has been demonstrated by nuclear magnetic resonance in 2-alkoxy-derivatives of chroman[86,139,140], 5,6-benzochroman[139], and dihydrophenanthro-1,4-dioxan[114]. Pfundt and Farid[114] observed with *trans*-2-ethoxy-5,6-dihydro-3-phenyl-5,6-phenanthro-1,4-dioxan (CVI) a mobile equilibrium with a considerable proportion of the diaxial conformation (CVII). Such a position of conformational equilibrium is undoubtedly due to a considerable decrease in ΔG_{Ph} on passing from oxan to dihydropyran derivatives. The *cis*-isomer exists as the conformation containing an axial ethoxy-group (CIX).



(CVI) (CVII) (CVIII)

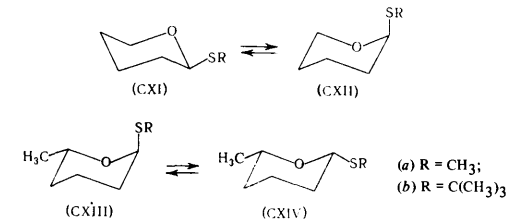
(CIX) (CX) (R = CH_3CO or C_6H_5CO)

Ferrier and Sankey[141] used nuclear magnetic resonance to show that, in esters of 2,3-didehydro-3-deoxyaldoses (CX), the allyl ester groups occupy preferentially (with respect to the double bond) a quasi-axial position, and the anomeric effect is 0.8 and 1.3 kcal mole^{-1} for the acetoxy- and benzoyloxy-groups respectively.

4. The O–C–S Fragment

(*a*) Alkylthio-derivatives of oxygen-containing heterocycles

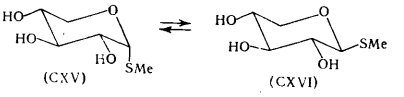
Semi-quantitative n.m.r. data have shown that 2-phenylthio- and 2-ethylthio-oxans possess an anomeric effect, although it is considerably weaker than in alkoxy-derivatives[54]. With 2-ethylthio-oxan, for example, the equilibrium mixture (in carbon tetrachloride) contains 65% of the axial isomer (CXII). This value agrees satisfactorily with results for the epimerisation of 2-methylthio- and 2-t-butylthio-6-methyloxans[56], the proportion of the axial *trans*-isomers (CXIII) being ~ 65% for both compounds. In acetonitrile, however, the equilibrium (CXIII) ⇌ (CXIV) is displaced in favour of the equatorial epimer, with values of ΔG of −0.08 and −0.12 kcal mole^{-1} for cases (*a*) and (*b*) respectively.



(CXI) (CXII)

(CXIII) (CXIV) (*a*) R = CH_3; (*b*) R = $C(CH_3)_3$

The epimerisation of methyl 1-deoxy-1-mercapto-β-D-ribopyranoside yields a mixture containing 18.5% and 7.4% respectively of the α- and β-epimers (CXV) and (CXVI), and thus suggests the presence of an anomeric effect. However, these results are not very exact, since the mixture contains a considerable proportion of furanoside forms[142]. 2-Ethylthiodihydrophenanthro-1,4-dioxan also exhibits an anomeric effect[114], the equilibrium content of the axial conformation being ~ 60%.

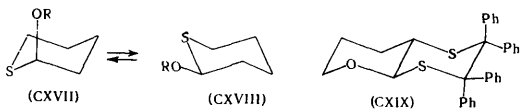


(CXV) (CXVI)

The above results show that the dipole interaction of oxygen and sulphur atoms is sufficient to destabilise the equatorial conformation.

(*b*) Alkoxythians

Since an anomeric effect is found with 2-alkylthio-derivatives of oxan, it should obviously occur also with alkoxylated six-membered sulphur-containing heterocycles. Zefirov et al. have shown[117,143] a distinct anomeric effect with 2-alkoxythians (CXVII) ⇌ (CXVIII). Thus the n.m.r. spectra indicate at least 90% of the isomer having the conformation (CXVII) at equilibrium in the cases of 2-methoxy- and 2-n-butoxy-thians, and the effect of solvents on the conformational equilibrium coincides with that observed for 2-alkoxyoxans[54,55].



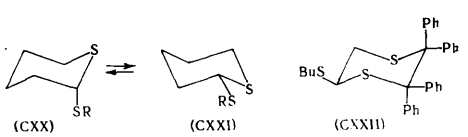
(CXVII) (CXVIII) (CXIX)

Distinct predominance of the axial conformation of alkoxy-derivatives has been found with 2-ethoxy- and 2-butoxy-5,5,6,6-tetraphenyl-1,4-dithians[144]. Thiobenzophenone reacts with dihydropyran to form *trans*-3,3,4,4-tetraphenyl-7-oxa-2,5-dithiabicyclo[4,4,0]decane (CXIX), the structure of which has been proved by n.m.r. spectroscopy[144,145]. In this connection it is of great interest to obtain the *cis*-isomer and also to study epimerisation.

It is interesting that according to the n.m.r. spectra[146] an anomeric effect occurs with thian-2-ol in deuterochloroform.

5. The S–C–S Fragment

Alkylthiothians (CXX) ⇌ (CXXI) exhibit a distinct anomeric effect[117], which has been estimated as 0.7 and 0.5 kcal mole^{-1} in carbon tetrachloride and in acetonitrile respectively.

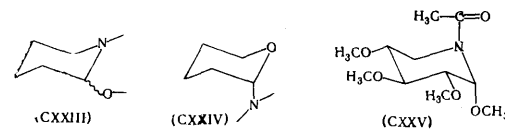


(CXX) (CXXI) (CXXII)

According to n.m.r. data, however, 2-butylthio-5,5,6,6-tetraphenyl-1,4-dithian exists predominantly as the equatorial conformation (CXXII).[144] This is probably due to strong 1,3-repulsion between phenyl and butylthio-groups, which predominates over the anomeric effect.

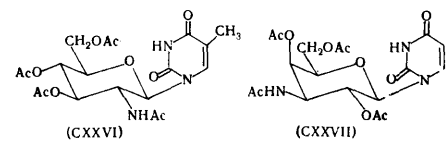
6. The N–C–O Fragment

The N–C–O fragment, containing an amino-nitrogen atom, can occur in two forms (CXXIII) and (CXXIV). In view of the variety of functional nitrogen groups, moreover, the conformational equilibrium of compounds of type (CXXIV) will obviously depend on the kind of nitrogen group present. Very few data are available on compounds of type (CXXIII).[147–149] Thus methyl *N*-acetyl-2,3,4-tri-*O*-methyl-α-D-xylopiperidinose occurs predominantly in the form (CXXV).[147] However, this effect may be due to purely steric factors (the conformation of 2-substituted *N*-acetylpiperidines will be discussed below). Compounds of type (CXXIV) containing an amino-group have been studied fairly thoroughly, but few data are available on the conformational equilibrium of such systems.



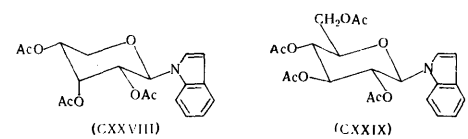
(CXXIII) (CXXIV) (CXXV)

A quite large number of examples have shown that substituents having an sp^2-hybrid nitrogen atom do not develop an anomeric effect. Thus epimerisation data for 1-(2-acetamido-3,4,6-tri-*O*-acetyldeoxy-β-D-glucopyranosyl)-thymine[150] and 1-(3-acetamido-2,4,6-tri-*O*-acetyl-3-deoxy-β-D-galactopyranosyl)uracil[151] indicate that the equatorial conformations (CXXVI) and (CXXVII) respectively are the more stable.



(CXXVI) (CXXVII)

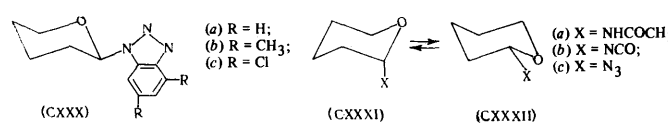
In a study of analogues of nucleosides Cushley et al.[152] discovered that an *N*-indolyl substituent on the $C_{(1')}$ atom of the pyranose ring also occupies the equatorial position, e.g. in



(CXXVIII) (CXXIX)

Similarly, the equatorial conformation (CXXX) is stable with benzotriazolyloxans[153].

A semi-quantitative estimate of the position of conformational equilibrium in *N*-oxan-2′-ylacetamide shows[104] that at least 85% of the conformation (CXXXII*a*) is present in the equilibrium (CXXXI) ⇌ (CXXXII).



(CXXX) (CXXXI) (CXXXII)

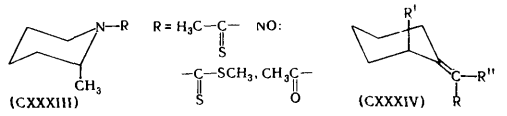
However, the situation changes markedly on passing to 2-substituted oxan derivatives containing linear functional groups in which nitrogen is present in the *sp*-hybrid state. Thus Zefirov and Shekhtman[104] showed by an n.m.r. method that the axial conformations (CXXXI*b*) and (CXXXI*c*) predominate at equilibrium in oxan-2-yl azide and isocyanate respectively, their proportions lying in the range 70–80%. It is interesting that, in the case of the azide, the proportion of the axial conformation diminishes on passing from acetonitrile to carbon tetrachloride.

7. The Fragments O–C–C, S–C–C, and N–C–C

The varied character of the functional groups containing a carbon atom makes it necessary to examine the conformational behaviour of compounds as a function of the type of hybridisation of the carbon atom. Consideration of the volume and electronegativity of the functional groups containing a tetrehedral carbon atom indicates absence of an anomeric effect with compounds containing simple alkyl groups. This principle is confirmed experimentally[154,155].

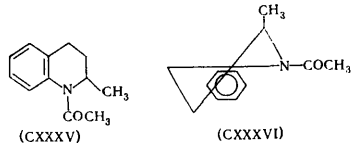
Anomalies might be expected with strong electron-acceptor groups such as trifluoromethyl and trichloromethyl, but experimental data on this aspect are lacking.

A very interesting phenomenon was discovered by Paulsen et al.[147,156,157], who found that a 2-methyl group in *N*-thioacetyl-, *N*-*syn*-nitroso-, *N*-methylthiothiocarbonyl-, and *N*-acetyl-piperidines occupies an axial position (CXXXIII). This phenomenon is most probably due not to a polar but to a steric effect. In fact, the cyclic nitrogen atom is trigonal in all the compounds, which produces strong steric repulsion between the *N*-substituents and the equatorial 2-methyl group.

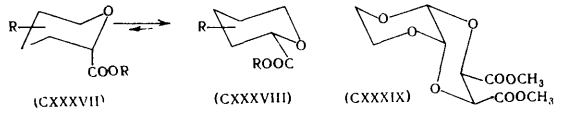


A similar effect has been found with cyclohexanes having an exocyclic double bond. Thus for compounds of type (CXXXIV) in which R = R′ = CH_3 the equilibrium mixture contains 85% of the axial conformations (CXXXIV).[158,159]

The methyl group in *N*-acetyltetrahydroquinaldine (CXXXV) has the axial conformation (CXXXVI).[155]



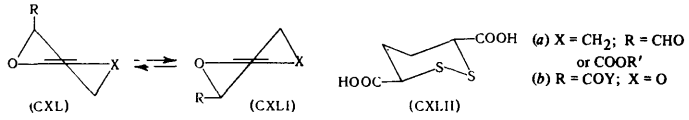
Available published data indicate that an anomeric effect is absent also from functional groups containing an sp^2-hybrid carbon atom. Thus epimerisation data on methyl alkyloxan-2-carboxylates (CXXXVII) ⇌ (CXXXIII) indicate that for the methoxycarbonyl groups ΔG = 1.62 kcal $mole^{-1}$.[160]



Using n.m.r. data Bramley et al.[161] showed that dimethyl decahydro-1,4,5,8-tetraoxanaphthalene-2,3-dicarboxylate has *cis*-fusion of the rings with a diequatorial arrangement of the methoxycarbonyl groups (CXXXIX).

A preferred equatorial position of methoxycarbonyl groups has been found also with isomeric methyl 6-alkoxyoxan-2-carboxylates[110,112].

Nuclear magnetic resonance has shown that the conformational equilibrium of 2-formyl- and 2-methoxycarbonyloxans is shifted towards the equatorial form (CXLI*a*).[137,162]



The absence of an anomeric effect in *trans*-1,2-dithian-3,6-dicarboxylic acid (CXLII) has been demonstrated by X-ray examination[163].

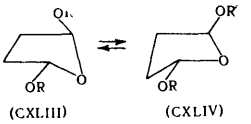
However, very interesting results have been obtained from a study of the conformational equilibrium of benzo-1,4-dioxan-2-carboxylic acid and its derivatives. The proportion of the axial conformation (CXL*b*) is 70%.[162,164] In this case the conformation is probably determined either by dipole–dipole attraction between the 4-heteroatom and the 2-functional group or by the inverse "hockey-stick effect", in which overlapping of the *p*-orbital of the carbon atom of the methoxycarbonyl group and the orbital of the 4:oxygen atm, which has a lone pair of electrons, leads to stabilisation of the axial conformation.

We may note in conclusion that data on functional groups having an *sp*-hybrid carbon atom are lacking, and therefore an experimental study of this question would be welcome.

IV. THE ANOMERIC EFFECT IN ACYCLIC AND NON-SIX-MEMBERED CYCLIC STRUCTURES

The anomeric effect should obviously apply to other types of structures containing an X–C–Y fragment.

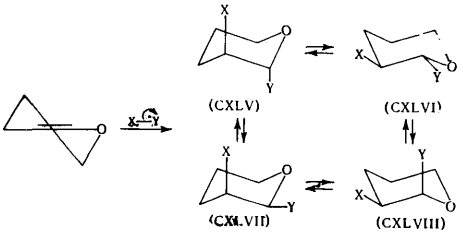
With cyclic structures interaction of this type should lead to stabilisation of the gauche conformation. Experimental data have shown that acetals exist predominantly in the gauche–gauche conformation[165], and a chloromethyl ether as a gauche conformation[166]. Polyformaldehyde, in contrast to polyethylene, forms a spiral chain[56,167].



A clear anomeric effect has been found in 2,5-dimethoxyoxolan[106]. Epimerisation in benzene yields an equilibrium mixture containing 63% of the *trans*-isomer (CXLIII). Increase in the polarity of the solvent shifts the equilibrium in favour of the *cis*-isomer (CXLIV). A similar situation has been found in 2-substituted 1,3-dioxolans[168]. This effect will obviously hold also for non-six-membered rings.

V. THE ANOMERIC EFFECT AS A FACTOR DETERMINING THE STEREOCHEMICAL COURSE OF REACTIONS

If a reaction is controlled thermodynamically, the anomeric effect will obviously be one factor determining the configuration of the products. This has already been shown in the examples of epimerisation. However, it applies also to certain other types of reactions. In particular, electrophilic addition at the double bond in Δ^2-dihydropyrans will lead under conditions of thermodynamic control to an appreciable quantity of a product having a *cis*-configuration. If a mechanism of *trans*-addition via the intermediate formation of an onium ion is accepted (for an alternative view see Ref. 169), the product will exist in the two conformations (CXLV) and (CXLVI). In this case epimerisation will yield the *cis*-isomer, which exists in the conformations (CXLVII) and (CXLVIII). In the absence of strong 1,2-repulsion between substituents X and Y to stabilise the conformation (CXLV), the conformation (CXLVIII) should obviously be the most stable. In fact, the halogenation of dihydropyran gives a mixture of *cis*- and *trans*-isomers[143,170], as discussed above, the proportion of the *cis*-isomer being greater in the dibromide than in the dichloride.



The addition of such electrophilic agents as nitrosyl chloride, oxalyl chloride, and acetals in the presence of boron trifluoride yields products having a *cis*-configuration of the type (CXLVIII).[169] The addition of ethanesulphenyl chloride to dihydropyran at low temperatures conforms to kinetic control and gives a normal product of *trans*-configuration, but at high temperatures the *cis*-isomer is obtained[171]. In the absence of added acid agents, which promote thermodynamic control, the formation of *trans*-products is more probable. In particular, as already noted above[55], the oxymercuration of dihydropyran yields the *trans*-isomer. It is noteworthy that *cis*-addition is very often observed in electrophilic additions at the double bond in polyfunctional derivatives of dihydropyran (glycals).[78,172-177]

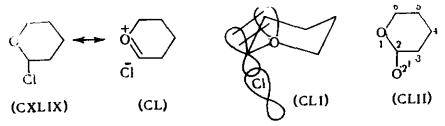
VI. THE NATURE OF THE ANOMERIC EFFECT

It is evident from the above discussion that an "anomeric effect" is exhibited by an extraordinarily wide range of compounds of various types and covers quite diverse phenomena. It therefore becomes necessary to refine this concept.

In a broad sense the term "anomeric effect" can be understood purely phenomenologically as the predominance of the axial conformation of a substituent in the α-position with respect to a heteroatom. Such an effect can obviously be due to a wide variety of causes, including purely steric factors, as has been discussed above for acetyl derivatives of piperidine.

In a narrower sense the anomeric effect can be understood as the predominance of an axial form as a consequence of specific non-steric interaction of a substituent with an adjacent heteroatom. This definition eliminates from discussion the effect of interaction of the substituent with a remote heteroatom, as discussed above for benzodioxan-2-carboxylic acid. In this sense the problem of the nature of the anomeric effect reduces to studying the interaction between the substituent and the heteroatom.

Two views are held on the nature of such interaction, according to one of which an explanation of the anomeric effect is to be sought in stereoelectronic factors. The concept of "double bond–no bond resonance"[178,180] is applied for this purpose. This concept has been used to explain various anomalies in the physical properties of compounds in which two electronegative substituents are attached to the same carbon atom. On this basis the resonance structures of 2-halogeno-oxans will be (CXLIX) and (CL).

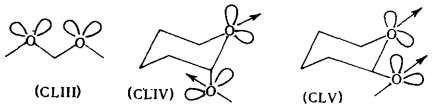


(CXLIX) (CL) (CLI) (CLII)

Such resonance is due to overlapping of the p_Z-orbital of the oxygen atom and the σ^*-orbital of the C–X bond (CLI).[7] The interaction between the p-electrons of the oxygen atom and the framework of σ-bonds for the fragment CH_2-O-CH_2-X has been examined[180-182]. Such overlapping will obviously be greatest with the halogen atom in the axial position. Therefore mixing of e.g. the p_Z-orbital of the ring oxygen atom and the σ^*-orbital of the carbon–halogen bond should result in stabilisation of the axial conformation. Conjugation of this type is supported by the shortening of the carbon–oxygen bond and lengthening of the C–X bond which are observed experimentally in several cases[183,184].

The situation is far more complicated, however, with alkoxy-derivatives[185-187]. Both the exocyclic $C_{(2)}-O_{(2')}$ bond (CLII) and in several cases also the $C_{(2)}-O_{(1)}$ bond are shortened. Shortening of the former bond has been observed also for the equatorial conformation[186,187].

Attempts have been made to relate the variation in bond lengths with the variation in angles and hence in hybridisation[187,188]. On the whole, however, this is a very complicated question, and a more detailed examination of this aspect of the "anomeric effect" encounters certain difficulties.



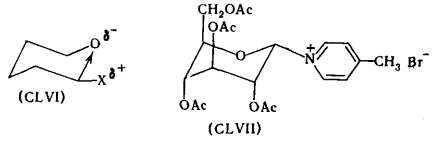
(CLIII) (CLIV) (CLV)

The second view relates the "anomeric effect" to dipole–dipole repulsion of substituent and heteroatom. The first to apply this idea was Edward[42]. Formulae (CLIV) and (CLV) show that dipole interaction is stronger in the equatorial than in the axial conformation. This view has been adopted in most papers. It is consistent with the influence of the solvent on the magnitude of the anomeric effect and with the qualitative changes observed with variation in the electronegativity of the substituent and the introduction of addition substituents[105,107,132]. Attempts have been made to calculate the electrostatic repulsion due to the dipole interaction[7]. However, although these calculations are consistent with the qualitative picture, they are unable to provide serious support for this view owing to the crudeness of the postulates involved.

A somewhat refined picture of such dipole–dipole interaction has recently become widespread. Since a considerable part of the negative charge is concentrated in the region of the lone pairs of the oxygen atoms, a rotational conformation of the type (CLIII) for the acetal fragment would be unstable. This phenomenon has been termed the "rabbit's-ears effect"[7-10]. An example is provided by the anomeric effect in alkoxyoxans. In several cases the "rabbit's-ears effect" enables the rotational conformations of alkoxy-groups to be predicted correctly, and it is applicable also to several nitrogen heterocycles and aliphatic compounds. In essence, however, this effect is also phenomenological, since the detailed causes of the instability of the conformation (CLIII) are unknown.

VII. THE INVERSE ANOMERIC EFFECT

In view of the polar nature of the anomeric effect, the converse effect can be imagined, in which there is dipole–dipole attraction between substituent and heteroatom of the type (CLVI). For a methyl alkyloxan-2-carboxylate, as noted above, $\Delta G_{COOR} = 1.62$ kcal mole^{-1},[160] which exceeds the value in methyl cyclohexanecarboxylate by 0.5 kcal mole^{-1}. Such an increase in the value of ΔG can be explained by two factors: a decrease in the distance between the atoms $C_{(2)}$ and $C_{(6)}$ in oxan will lead to an increase in 1,3-diaxial repulsion between the 6-hydrogen atom and the 2-substituent; it is also possible that this difference is due to an inverse anomeric effect.



(CLVI) (CLVII)

The clearest example of an inverse anomeric effect was observed by Lemieux and Morgan[189] with a glucopyranosylpyridinium salt. According to n.m.r. data this compound exists as the conformation (CLVII), in which the three acetoxy-groups and the acetoxymethyl group are present in axial conformations. Stabilisation of such a conformation is obviously due to an inverse anomeric effect—attraction of the heteroatom and the equatorial pyridinium group. Obviously, although very little study has been made of the inverse anomeric effect, it should also be a general phenomenon, applying to a wide range of compounds.

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As the present Review has shown, the anomeric effect is a general conformational phenomenon covering an extraordinarily wide range of compounds. Although the nature of this effect is a matter of controversy, we are able to predict it with a considerable degree of probability for a large number of compounds which have not yet been studied. It is quite obvious that further investigation of this effect with the use of new model compounds and a more profound study will lead to progress in understanding the nature of the forces determining the conformations of molecules.

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Advances in the Synthesis of Glycerol Phosphatide Esters

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A survey is given of the present position in the synthesis of glycerol phosphatide esters—phosphoric esters in which the glycerol residue is esterified—some of the principal representatives of the biologically important class of substances, the lipids. The main principles and recent advances are discussed in the synthesis of classical glycerol phosphatide diesters of the type of cephalins, lecithins, phosphatidylserines, cardiolipins, phosphatidylglycerols and their amino-acid derivatives, etc., and also complex phosphatides containing amino-acids, peptides, and sugars. Special attention is paid to the synthesis of optically active unsymettrically substituted myoinositols, which include such glycerol phosphatides as mono-, di-, and tri-phosphoinositides and complexes based on them. The list of references includes 246 items.

I. INTRODUCTION

During the past twenty years the chemistry of the important natural compounds the lipids, including that of glycerol phosphatide esters, has made great advances, with the possibility of finally determining the structure of the principal classical glycerophosphatide esters—phosphatidic acids, phosphatidylaminoethanols (cephalins), phosphatidylcholines (lecithins), phosphatidylserines, phosphoinositides of various types (mono-, di-, and tri-phosphoinositides) phosphatidylglycerols, diphosphatidylglycerols (cardiolipins), amino-acid derivatives of phosphatidylglycerol, etc.[1,2]

To a considerable extent this enabled the problem of studying the part played by glycerophosphatides in processes occurring in the living cell (membrane processes, the chain of electron transfer, the transmission of nerve impulses, metabolic mechanisms, etc.) to be raised to the molecular level, which promises in the near future to solve many fundamental questions of biology where an important role is assigned to glycerophosphatides[3].

Synthetic work in the field of glycerophosphatides has made one of the principal contributions to their chemical investigation. The main lines of these researches were shown in several reviews[4-12], which were devoted to individual aspects of the synthetic chemistry of glycerophosphatides and hence did not give a complete picture. Furthermore, most of them almost completely ignore work in the Soviet Union on the synthesis of glycerophosphatides, which is being widely developed at the present time and in many respects has enriched considerably our knowledge of their chemistry. These were the main reasons for publishing the present Review.

The synthesis of glycerophosphatides reached its present level in effect only during the past decade in connection with the widespread introduction into the chemistry of lipids of physicochemical methods for purifying and identifying organic compounds and establishing their structure. In this sense an important part in the advances of recent years has been played by adsorption, paper, thin-layer, and gas–liquid chromatography, infrared spectroscopy, and recently mass spectroscopy, nuclear magnetic resonance (n.m.r.), and optical rotatory dispersion.

Nowadays the synthesis of diester glycerophosphatides such as cephalins, lecithins, and phosphatidylserines—which are often termed classical—presents no difficulty, largely owing to recent advances in the synthesis of triester glycerophosphatides[13-15], phosphatidopeptides[16-21], and other complex glycerophosphatides[22-26], papers on whose isolation from natural sources have begun to appear.

The methods now used for the preparation of glycerophosphatides consist in the successive building up of individual structural parts of the molecule (phosphoric esters of the nitrogen bases and amino-acids, aliphatic acids, etc.) from various derivatives of unsymmetrically substituted glycerol.

All the methods which have been described for synthesising glycerophosphatides can be divided into two broad groups: (1) synthesis from 1,2-diglyceride structures presupposes the initial production of the 1,2-diglyceride part of the molecule, so that in this case the introduction of aliphatic acids into a substituted glycerol molecule precedes phosphorylation; (2) the synthesis from glycerophosphoric esters is characterised by the opposite sequence of esterification and phosphorylation.

II. SYNTHESIS OF GLYCEROPHOSPHATIDES FROM 1,2-DIGLYCERIDE STRUCTURES

This group of preparations includes two independent methods. A common feature is the initial production of a 1,2-diglyceride structure either in the form of a 1,2-diacyl-*sn*-glycerol† or as a 1,2-diacyl-3-deoxy-3-iodo(or bromo)-*sn*-glycerol. Phosphoric ester bonds are formed with the first group of compounds by well known methods of phosphorylation[27], and with the second group by reaction with the silver salts of substituted phosphoric acids[28].

† The nomenclature of optically active unsymmetrically substituted glycerol derivatives conforms to the IUPAC–IUB rules—European J. Biochem., 2, 127 (1967).

1. Synthesis of 1,2-Diglycerides

The preparation of 1,2-diglycerides presents considerable difficulties, owing to the greater reactivity of the 1,3-hydroxy-groups of glycerol in comparison with the 2-hydroxyl, and also because of the ease of migration of acyl groups from the 2-position to the 1- and 3-positions[29]. Therefore many of the earlier published syntheses of 1,2-diglycerides did not yield pure compounds but mixtures of 1,2- and 1,3-diglycerides. These facts have necessitated special approaches to the preparation of 1,2-diglycerides which would avoid these difficulties.

One approach is the temporary protection of the 3-hydroxyl. The methods used most frequently have been benzyloxycarbonyl[30], trityl[31-35], benzyl[39], oxanyl[34,37], ethoxyethyl[34], and 2,2,2-trichloroethoxycarbonyl[38,39] protection. The 3-*O*-derivatives of glycerol were esterified either in stages or exhaustively, and at the last stage the protecting group was removed by catalytic hydrogenolysis[30-32,36] or mild acid hydrolysis, excluding migration of the aliphatic acid radicals[33-35,38,39]. This yielded 1,2-diglycerides containing the same or different acids. The problem of the selective introduction of different aliphatic acid radicals and also the possibility of obtaining highly unsaturated 1,2-diglycerides will be specially considered in subsequent sections.

Another approach to the preparation of 1,2-diacylglycerols consists in using 2-monoglycerides obtained by removing benzylidene protecting groups by catalytic hydrogenolysis[40,41] or mild hydrolysis with boric acid[42,43] of the corresponding acyl derivatives of 1,3-*O*-benzylideneglycerol. 2-Monoglycerides are selectively esterified to 1,2-diglycerides. The method makes it possible to obtain racemic 1,2-diglycerides of any structure and degree of unsaturation.

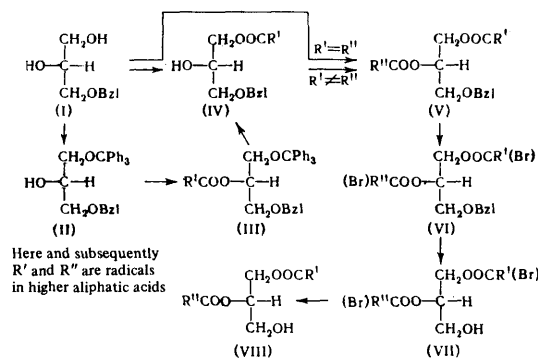
None of the above methods is universally applicable: with some of them it is impossible (or possible in only a few cases) to obtain 1,2-diglycerides containing the radicals of highly unsaturated aliphatic acids[30-32,36], which are widely distributed in natural sources and are of the greatest biological value[1,2]; other methods are unsuited to the preparation of optically active 1,2-diacyl-*sn*-glycerols[30-33,37,44-47], in the form in which they are involved in various biological processes in the living cell[1,2].

Further discussion of synthetic approaches to 1,2-diglycerides will be arranged to show which methods are most suitable for the preparation of saturated and unsaturated 1,2-diacyl-*sn*-glycerols containing the same and different acid radicals. These compounds have been prepared most often by the benzyl method, which was proposed for saturated 1,2-diglycerides[36].

Hydrogenation of ethylenic double bonds in acyl radicals during the preparation of unsaturated 1,2-diglycerides, which would occur on catalytic debenzylation (VI) → (VII), is avoided by preliminary protection with bromine (V) → (VI). Debenzylation is followed by debromination with zinc dust (VII) → (VIII), which restores the original double bonds, without change in their configuration, to give the 1,2-diacyl-*sn*-glycerols (VIII)[48-57] (Scheme 1).

Diglycerides containing different acid radicals can be prepared in two ways, distinguished by the methods used to introduce aliphatic acids into the 1- and 2-positions—(i) acylation in stages (I) → (IV) → (V)[51,52,54,56,57] [direct esterification (I) → (V) yields diglycerides containing the same acid radicals[48,50,52,55]], and (ii) preliminary protection of the 1-hydroxyl with a trityl radical (I) → (II), which, after introduction of an aliphatic acid radical on the 2-hydroxyl (II) → (III), is removed by means of hydrogen chloride with migration of the acyl radical from the 2- to the 1-position (III) → (IV), this being followed by esterification of the freed 2-hydroxyl (IV) → (V).[49,53,54]

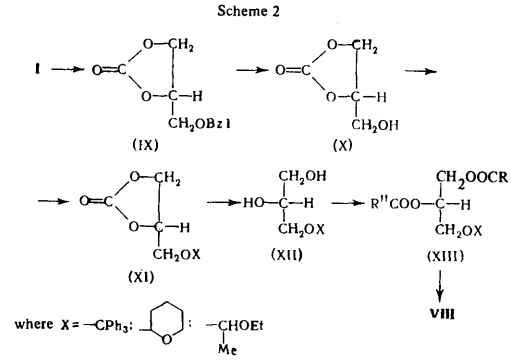
Scheme 1



With highly unsaturated aliphatic acids such as linoleic and linolenic acids the benzyl method of preparing diglycerides has considerable limitations[50-57], and it is entirely unsuitable for the preparation of 1,2-diacyl-*sn*-glycerols containing still more highly unsaturated acid radicals, e.g. from arachidonic acid. This is because a large quantity of bromine introduced at the double bonds in the aliphatic acid leads to difficulties in debenzylation owing to poisoning of the catalyst, and also because of the poor solubility of the bromides which are formed. Several attempts have been made recently to modify the benzyl method of preparing 1,2-diglycerides with the aim of applying it to obtain 1,2-diacyl-*sn*-glycerols of any degree of unsaturation.

The first of these attempts consists in replacing the benzyl protection in 3-*O*-benzyl-*sn*-glycerol (I) by a trityl, an oxanyl, or an ethoxyethyl group (I) → (XII). These groups are easily removed by mild acid hydrolysis of compounds of type (XIII)—obtained by the esterification of 3-*O*-derivatives of *sn*-glycerol (XII)—with the formation of 1,2-diglycerides (VIII) (Scheme 2).[34]

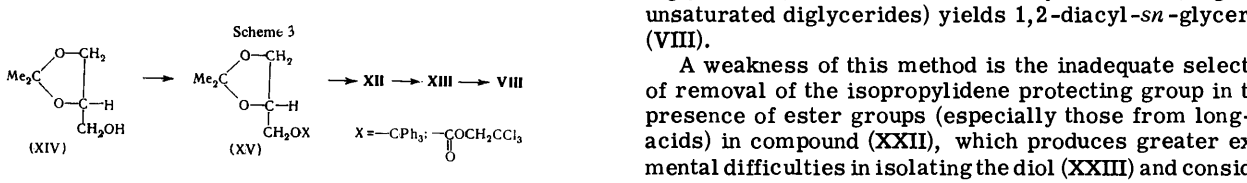
Scheme 2



Other papers[35,38,39] also propose replacing the benzyl group in 3-*O*-substituted glycerol (XII) by groups more suitable for the preparation of highly unsaturated 1,2-diglycerides, such as trityl[35] and 2,2,2-trichloroethoxycarbonyl[38,39] (the former is removed by chromatography on

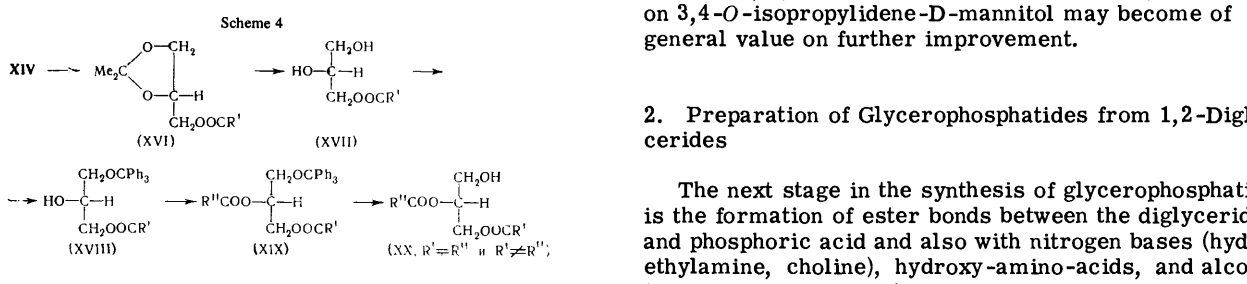
silicic acid[33], and the latter with zinc in acetic acid[38,39]) (Scheme 3).

Scheme 3



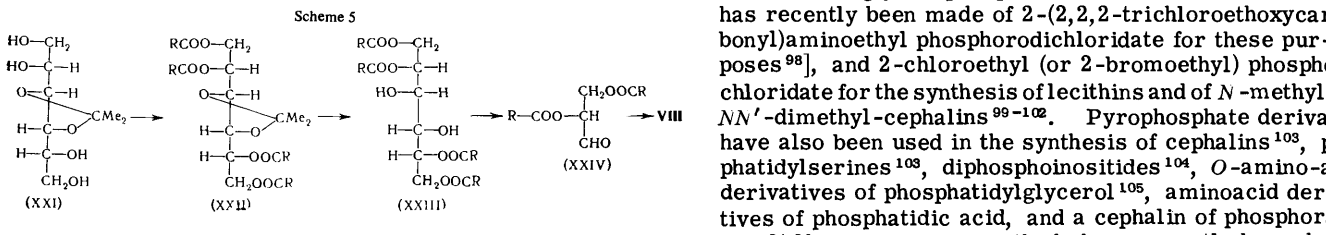
The chief difficulty in these syntheses is to remove isopropylidene protecting groups‡ in the presence of trityl and 2,2,2-trichloroethoxycarbonyl groups (XV) → (XII): in the first case[35] this is achieved by the action of trichloroacetic acid, and in the latter case with boric acid[38,39]. Since both isopropylidene and the two other protective groups[35,38,39] are sensitive to acid hydrolysis, although in differing degrees, it is difficult to rely on complete selectivity of removal of the acetal group, which considerably diminishes the potentialities of this method.

Scheme 4



Attempts to replace benzyl by trityl protecting groups had been made earlier (Scheme 4).[56,58] The diglycerides were prepared from 1,2-*O*-isopropylidene-*sn*-glycerol (XIV), which was converted into the 3-monoglyceride (XVII), then subjected to tritylation and complete acylation (XVII) → (XVIII) → (XIX), and after removal of the trityl protecting group under mild conditions[33] converted, as was to be expected, into the enantiomer of the natural diglyceride, 2,3-diacyl-*sn*-glycerol (XX). The preparation of 1,2-diacyl-*sn*-glycerols by this method from L-mannitol as starting material (D-mannitol was used in the other preparations) was impracticable because of the great shortage of L-mannitol.

Scheme 5



Finally, a new method has recently been suggested for preparing 1,2-diacyl-*sn*-glycerols[59], in which the starting material is 3,4-*O*-isopropylidene-D-mannitol (XXI), which is obtained from D-mannitol via the intermediate formation of 1,2 : 3,4 : 5,6-tri-*O*-isopropylidene-D-mannitol (Scheme 5).[60] Esterification converts (XXI) into the tetra-acyl derivative (XXII). After mild acid hydrolysis of the acetal protecting group the diol (XXIII) is oxidised with lead tetra-acetate to the 1,2-diacyl-*sn*-glyceraldehyde (XXIV). Reduction of (XXIV) with hydrogen in the presence of Raney nickel (for the preparation of saturated diglycerides) or with sodium tetrahydroborate (to give unsaturated diglycerides) yields 1,2-diacyl-*sn*-glycerols (VIII).

A weakness of this method is the inadequate selectivity of removal of the isopropylidene protecting group in the presence of ester groups (especially those from long-chain acids) in compound (XXII), which produces greater experimental difficulties in isolating the diol (XXIII) and considerably diminishes the overall yield of the diglyceride (VIII).

Summarising this Section, we can say that, in spite of the great amount of work on the preparation of 1,2-diacyl-*sn*-glycerols, no method can be suggested at the present time which would be universally applicable to products of any structure and degree of unsaturation. Nevertheless, some specialisation of methods is possible. The benzyl method is the most suitable for obtaining saturated and slightly unsaturated diglycerides. The carbonate method is to be recommended for the preparation of highly unsaturated diglycerides. Finally, methods based on 3-*O*-trityl- or 3-*O*-2′,2′,2′-trichloroethoxycarbonyl-*sn*-glycerols and on 3,4-*O*-isopropylidene-D-mannitol may become of general value on further improvement.

2. Preparation of Glycerophosphatides from 1,2-Diglycerides

The next stage in the synthesis of glycerophosphatides is the formation of ester bonds between the diglycerides and phosphoric acid and also with nitrogen bases (hydroxyethylamine, choline), hydroxy-amino-acids, and alcohols (glycerol, myoinositol).

Phosphorylation is most often effected with phenyl phosphorodichloridate[61-74] and phosphoryl chloride[39,57,75-93] in the cases of saturated and unsaturated compounds respectively. Use of the latter agent lowers the yield of the final glycerophosphatides owing to formation of a large quantity of by-products. Compounds of the required structure are isolated from the complicated reaction mixture mostly by chromatography on silicic acid.

There are several modifications of phosphorylation, which make it possible to achieve unambiguous results in certain particular cases. Thus 2-phthalimidoethyl phosphorodichloridate has been used for the synthesis of cephalins and triester glycerophosphatides[13-15,21,44,47,55,58,94-97] [use has recently been made of 2-(2,2,2-trichloroethoxycarbonyl)aminoethyl phosphorodichloridate for these purposes[98]], and 2-chloroethyl (or 2-bromoethyl) phosphorochloridate for the synthesis of lecithins and of *N*-methyl- and *NN*′-dimethyl-cephalins[99-102]. Pyrophosphate derivatives have also been used in the synthesis of cephalins[103], phosphatidylserines[103], diphosphoinositides[104], *O*-amino-acid derivatives of phosphatidylglycerol[105], aminoacid derivatives of phosphatidic acid, and a cephalin of phosphoramide type[24,26]. Interesting methods have recently been developed for producing bonds of the type P—O—nitrogen base (the latter is usually aminoethanol). Among them are the reactions of phosphatidic acids with aziridine and its derivatives[106,107], and also with nitrogen bases in the presence of trichloroacetonitrile[39], 2,4,6-tri-isopropylbenzenesulphonyl chloride[108], and dicyclohexylcarbodiimide[109]. This last reagent has also been used to obtain phosphatidylglycerol and dipyrophosphatidic acid from phosphatidic acid[93,100].

In order to ensure an unambiguous result of phosphorylation, all the functional groups, other than the hydroxyls

‡ See next paragraph (Editor of Translation).

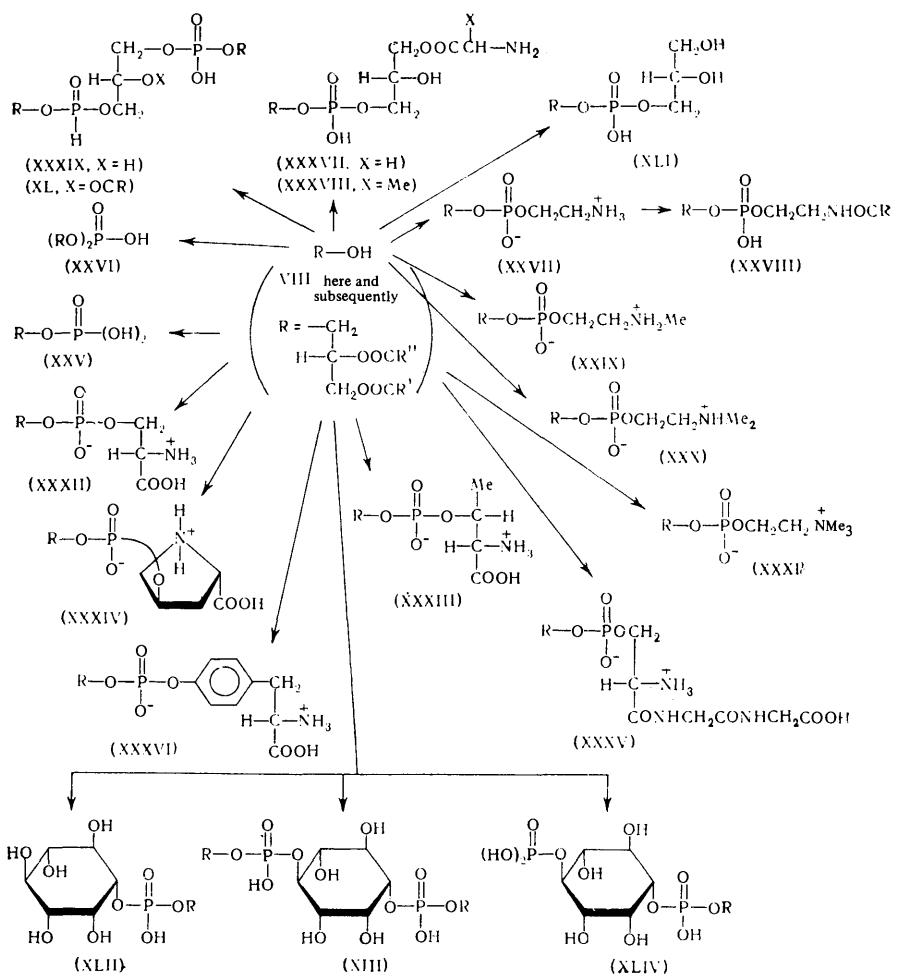
to be phosphorylated, in the nitrogen bases, hydroxy-amino-acids, glycerol, and myoinositol are blocked with protective groups. Amino-groups are protected with benzyloxycarbonyl [13,14,19,25,64,66-72,85], phthaloyl [13-15,44,45,47,55,58,77,78,84,86,94-97,105], t-butoxycarbonyl [39,81,83,90,91,109], methoxybenzyloxycarbonyl [92], 2,2,2-trichloroethoxycarbonyl [98], and γ-chlorobutyroyl [87] groups. The carboxy-groups of the amino-acids are blocked with benzyl [15,24,26,66,67,69,70,103], t-butyl [83,86,90], and phthalimidomethyl [81,87,92] protecting groups; and the hydroxyl of glycerol and myoinositol with benzyl [73,88,105,111-113], t-butyl [91], isopropylidene [75], cyclohexylidene [104,114], acetyl [13,16,21,115], benzoyl [104,116,117], toluene-*p*-sulphonyl [118,119], and oxanyl [111,116] groups.

Protective benzyloxycarbonyl, benzyl, and toluene-*p*-sulphonyl groups are removed in the last stages of hydrogenolysis, which excludes their application to the preparation of unsaturated glycerophosphatides. However, the methods which have appeared for the mild electrochemical removal of these groups will undoubtedly enable the limitations on their protective use to be overcome [20,120,121]. The conditions under which the remaining protective groups are eliminated enables them to be recommended for the preparation of both saturated and unsaturated glycerophosphatides. Thus phthaloyl, phthalimidomethyl, acetyl, and benzoyl groups are split off by mild hydrazinolysis, t-butyl, t-butoxycarbonyl, methoxybenzyloxycarbonyl, γ-chlorobutyroyl, isopropylidene, cyclohexylidene, and oxanyl groups by mild acid hydrolysis; and the 2,2,2-trichloroethoxycarbonyl radical with zinc in acetic acid.

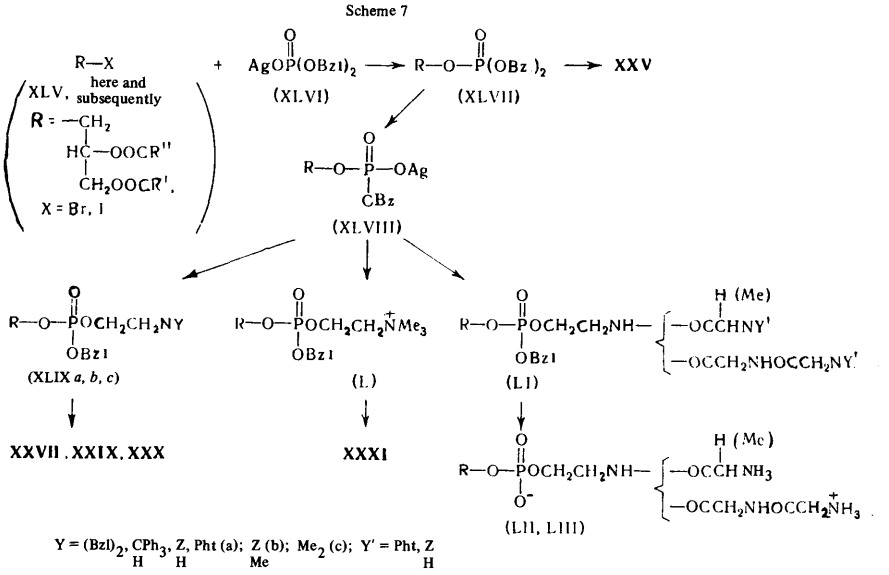
The wide choice of means of protection and phosphorylating agents enables glycerophosphatides of any structure to be obtained, provided that such structure was present in the initial diglycerides and also in the second structural unit of the phosphatide (nitrogen base, hydroxy-amino-acid, glycerol, myoinositol, etc.).

As is shown by Scheme 6, many glycerophosphatides have now been prepared, including phosphatidic acids (XXVI), [65,75,76,82,89,92,93,110,122,123] cephalins (XXVII), [39,44,45,47,55,58,63,64,77,78,84,85,94-98,103,107-109] on the basis of which have recently been obtained *N*-acyl-cephalins (XXVIII), [124] *N*-methylcephalins (XXIX), [68,101,108] *NN'*-dimethylcephalins (XXX), [57,101,108] lecithins (XXXI), [61,62,79,80,99,100,102] phosphatidylserines (XXXII), [66,81,83,89,87,130] and also several phosphatides containing threonine (XXXIII), [70] hydroxyproline (XXXIV), [69,92] and serylglycylglycine (XXXV). [97] Effectively the same methods have been used to obtain the highly unsaturated compounds phosphatidyltyrosine (XXXVI), [90] *O*-amino-acid derivatives of phosphatidylglycerol (XXXVII) and (XXXVIII), [73,91,105]

Scheme 6



Scheme 7



cardiolipin and its acyl derivatives (XXIX) and (XL),[88,89] phosphatidylglycerols (XLI),[75,88,110] and also racemic monophosphoinositides (XLII)[115] and diphosphoinositides of various structures (XLIII) and (XLIV)[104,114] (the preparation of optically active phosphoinositides will be discussed separately).

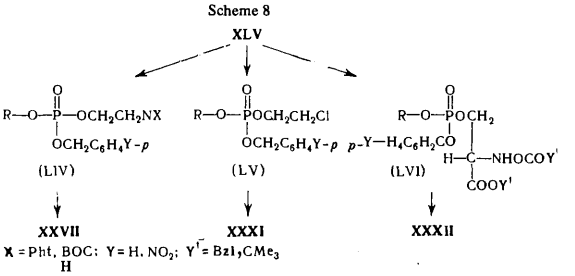
This method has also been used to prepare several modified glycerophosphatides containing 2-aminopropan-1-ol,[72] 2-amino-2-methylpropan-1-ol,[71] α-methylcholine[74], and certain cytotoxic groups[125].

3. Preparation of Glycerophosphatides based on 1,2-Diacylhalogenohydrins of *sn*-Glycerol

The preparation of 1,2-diacylhalogenohydrins of *sn*-glycerol presents considerably fewer difficulties than that of 1,2-diglycerides. They are prepared from 1,2-*O*-isopropylidene-*sn*-glycerol (XIV) in a series of stages, the last of which is esterification. Replacement of the hydroxyl by a halogen (iodine, bromine) is accomplished by the use of toluene-*p*-sulphonyl derivatives as intermediates[28,126-130]. Phosphoric ester bonds are then produced by the reaction of 1,2-diacylhalogenohydrins of *sn*-glycerol with silver salts of substituted phosphoric acids[28].

The synthesis can be effected in two ways. In the first case (Scheme 7) the reaction of 1,2-diacylhalogenohydrins of *sn*-glycerol (XLV) with silver dibenzyl phosphate (XLVI) yields dibenzyl phosphatidates (XLVII), which after anionic monodebenzylation with sodium iodide, lithium fluoride, or a similar reagent[131] are converted into alkali-metal salts, and then into the silver benzyl phosphatidates (XLVIII). These last products react with halogeno-derivatives of nitrogen bases to form protected glycerophosphatides (XLIX)–(LI). The benzyl group (sometimes *p*-nitrobenzyl is used instead) is removed by catalytic hydrogenolysis or by further anionic debenzylation, which in this case can be conveniently accomplished with a tertiary base such as *N*-methylmorpholine. The same groups are used to block amine and carboxyl functions as in the preparation of glycerophosphatides from 1,2-diglycerides. The benzyl[132-134] and trityl[135] groups are also used to protect amino-groups. This variant has proved most convenient for preparing several phosphatidic acids (XXV),[28,130,136-140] cephalins (XXVII),[128,132-135,141] *N*-methylcephalins (XXIX),[135] *NN'*-dimethylcephalins (XXX),[142] lecithins (XXXI),[127,128,143-145] and also phosphatidopeptides (LII) and (LIII).[17-20] Series of lysophosphatides such as lysocephalins and lysolecithins have been obtained similarly[146,147].

Scheme 8



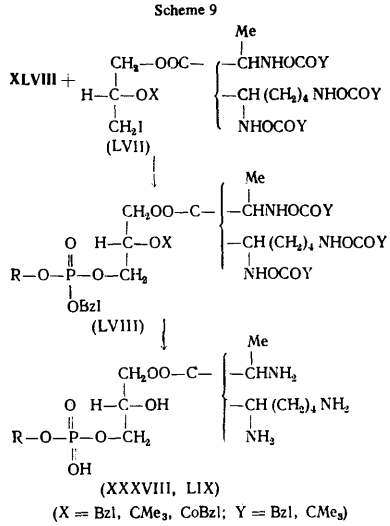
In the second form of the method (Scheme 8) molecules of protected glycerophosphatides (LIV)–(LVI) are produced by condensing the 1,2-diacylhalogenohydrin of *sn*-glycerol (XLV) with a silver salt of a substituted phosphoric acid in which a phosphoric ester bond has already been established with a nitrogen base or with serine.

Differences in principle between these methods are slight. The latter variant has found application also in the synthesis of cephalins (XXVII),[129,127,148-153] lecithins (XXXI),[154] and also, in contrast to the first variant, to obtain phosphatidylserines (XXXII).[126,155,156] This method of synthesis has proved especially convenient for obtaining highly unsaturated phosphatides[148-154,156], amino-groups being protected by means of the t-butoxycarbonyl group[151,156], and the carboxyl function by means of a t-butyl group[156].

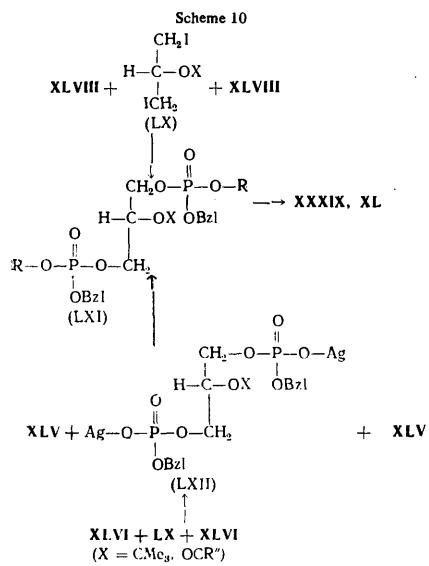
Double decomposition between derivatives of glycerol iodohydrin and silver salts of phosphoric acids is widely used in the preparation of *O*-amino-acid derivatives of phosphatidylglycerol. The method has found application in obtaining both unsaturated[91,157,158] and saturated compounds with individual parts of the molecule differing in configuration[159-161]. It consists in condensing silver benzyl phosphatidates (XLVIII) with glycerol iodohydrins

protected in the 2-position and esterified in the 1- or 3-position with protected amino-acids (LVII). As usual, the protected groups are removed at the last stage: (LVIII) → (XXXVIII), (LIX) (Scheme 9).

Scheme 9



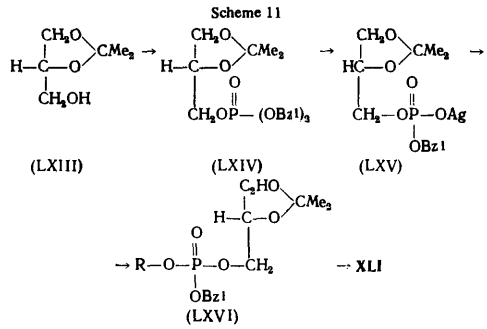
Scheme 10



The same principle forms the basis of a synthesis of cardiolipin (XXXIX) and its *O*-acyl derivatives (XL) [162,163] (Scheme 10). The molecular structures (LXI), containing three glycerol residues linked by phosphoric acid, were produced either by the reaction of two molecules of silver benzyl phosphatidate (XLVIII) with 2-*O*-t-butyl(or acyl)-1,3-deoxy-1,3-di-iodoglycerol (LX) or by combining two molecules of 1,2-diacyliodohydrins of *sn*-glycerol (XLV) with the disilver salt of 2-*O*-t-butyl(or acyl)glycerol 1,3-bis(benzyl phosphate) (LXII), obtained by the reaction of (LX) with silver dibenzyl phosphate (XLVI) followed by partial debenzylation and conversion into the corresponding silver salt (LXII). The protecting groups were removed in the usual way as the final stage: (LXI) → (XXXIX), (XL).

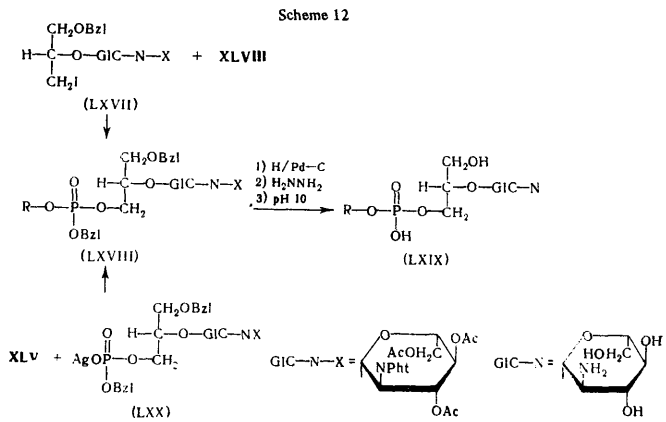
Phosphatidylglycerol (XLI) has been synthesised by a similar method [164] (Scheme 11).

Scheme 11



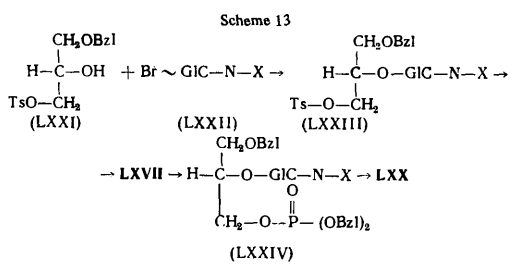
During recent years the present method has been used for the preparation of several glycolipids. The first synthetic work on these lines was concerned with a glucosamine derivatives of phosphatidylglycerol (LXIX) [22]—a glycolipid found in *Bacillus megatherium* [23,165] (Scheme 12).

Scheme 12



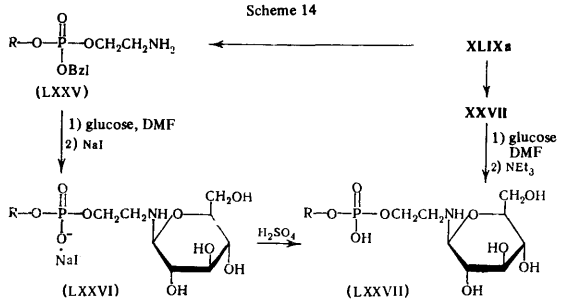
A glycosidic bond between the anomeric hydroxyl of the glucosamine and the 2-hydroxyl of glycerol was formed by the Koenigs–Knorr reaction of the corresponding glycerol derivatives (LXXI) and the glucosamine bromide (LXXII). The product (LXXIII) was converted by well known methods into the halogenohydrin (LXVII) and the silver salt (LXX), which were used as the chief intermediates in the synthesis of a glucosamine derivative of phosphatidylglycerol (LXIX) (Scheme 13).

Scheme 13



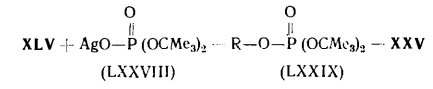
Another example is the synthesis of the *N*-glycoside of aminoethyl phosphatidate (LXXVII) [166] based on synthetic cephalin (XXVII) [135] (Scheme 14).

Scheme 14



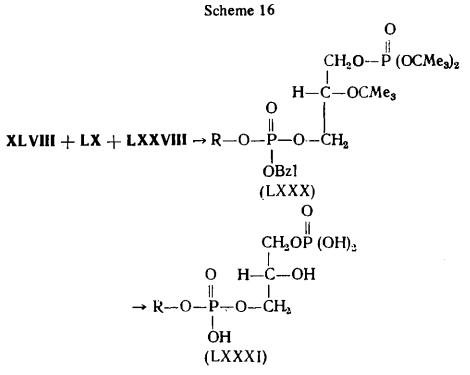
A further development of the method is to use silver di-t-butyl phosphate (LXXVIII) as phosphorylating agent in cases in which phosphoric monoesters are to be prepared, because of the ease of removal of a t-butyl group with hydrogen chloride (Scheme 15). Thus phosphatidic acid (XXV) has been obtained by the reaction of 1,2-diacyliodohydrin of *sn*-glycerol (XLV) with the above silver salt (LXXVIII). [167]

Scheme 15



The same silver salt (LXXVIII) has been used for the synthesis of phosphatidyl glycerophosphate (LXXXI) [167] by condensation with silver benzyl phosphatidate (XLVIII) and glycerol di-iodohydrin (LX) followed by removal of the protecting group (Scheme 16).

Scheme 16



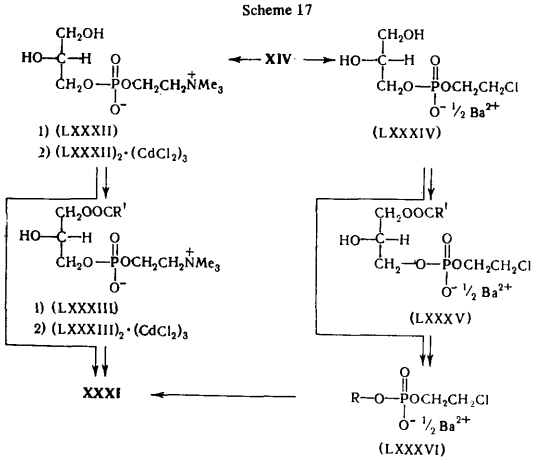
The method of preparing phosphatides by double decomposition of various glycerol halogenohydrins with silver salts of derivatives of phosphoric acids is distinguished from syntheses based on 1,2-diacyl-*sn*-glycerols by its directional character and hence by higher yields of reactions involving the formation of phosphoric ester bonds. However, it is also characterised by many stages and serious experimental difficulties in obtaining many of the starting materials, which often prevent it from competing with the preparation of phosphatides from 1,2-diglycerides.

III. SYNTHESIS OF GLYCEROPHOSPHATIDES BY THE ACYLATION OF SUBSTITUTED GLYCEROPHOSPHORIC ACIDS

The first group of methods for synthesising glycerophosphatides is characterised by several stages, which often diminishes its preparative possibilities. The second type of synthesis, in which the sequence of phosphorylation and acylation is reversed compared with the first group, enables diester glycerophosphatides to be obtained by a shorter route and in high yields directly from 1,2-*O*-isopropylidene-*sn*-glycerol (XIV).

It must be borne in mind that the esterification of glycerophosphoric esters of protected aminoethanol, choline, and serine occurs with considerable difficulty and yields mainly lysophosphatides [62,168,169]. During recent years, however, methods have been found which have permitted the selective or exhaustive esterification of glycerophosphoric esters of nitrogen bases [145,169-192]. The starting material mostly used for this purpose in the synthesis of lecithins (XXXI) has been either the cadmium complex of 3-*sn*-glycerylphosphorylcholine 2(LXXXII).$.3CdCl_2$ [145,169,171-177,179] or barium chloroethyl 3-*sn*-glyceryl phosphate (LXXXIV), [170,178] both obtainable by accessible methods from 1,2-*O*-isopropylidene-*sn*-glycerol (XIV). The compounds—(LXXXII), 2(LXXXII).$3CdCl_2$, (LXXXIII), 2(LXXXIII).$3CdCl_2$, (LXXXIV), and (LXXXV)—were acylated either selectively or exhaustively with aliphatic acid chlorides [169-179] or by enzymatic esterification [180,181]. In the case of the cadmium complexes [145,169,171-177,179] this immediately yields lecithins (XXXI) or lysolecithins (LXXXIII) depending on the degree of esterification. When the barium salts (LXXXIV) and (LXXXV) are used [170,173], the quaternary ammonium group of the lecithins (XXXI) is introduced by reaction between the acylated barium salt (XXXVI) and trimethylamine (Scheme 17).

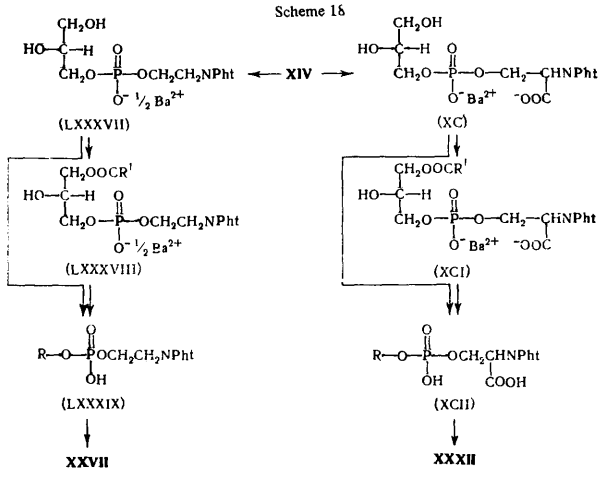
Scheme 17



In the synthesis of cephalins (XXVII) [182-185] and phosphatidylserines (XXXII) [186] from 1,2-*O*-isopropylidene-*sn*-glycerol (XIV) barium 3-*sn*-glyceryl *N*-phthaloylaminoethyl phosphate (LXXXVII) and the corresponding *N*-phthaloylserine salt (XC) are obtained. These are converted by stepwise esterification—(LXXXVII) → (LXXXVIII) → (LXXXIX) or (XC) → (XCI) → (XCII)—or complete esterification—(LXXVII) → (LXXXIX) or (XC) → (XCII)—into phthaloyl derivatives of cephalin (LXXXIX) or

phosphatidylserine (XCII), from which the protective groups are removed by mild hydrazinolysis (XXVII) or (XXXII) (Scheme 18). A similar principle has been used to obtain an unsaturated phosphatidylserine from barium glyceryl *N*-methoxybenzyloxycarbonylserine phosphate or the phthalimidomethyl ester[187].

Scheme 18



Besides being shorter than the first group of methods, the present route for the synthesis of glycerophosphatides has the advantage of being universally applicable for the preparation of phosphatides containing either saturated or unsaturated aliphatic acids.

Attempts have been made at the direct acylation of glycerophosphoric esters of nitrogen bases by means of acid anhydrides. Although the first work of this type[188] has only historic significance, later investigations on the acylation of 3-*sn*-glycerophosphate[189], 3-*sn*-glyceryl-phosphoryl-*N*-phthaloylaminoethanol[190] obtained by saponifying natural cephalins and then protecting the amino-group with a phthaloyl group, and 3-*sn*-glyceryl-phosphorylcholine[191,192] with aliphatic acid anhydrides in the presence of their tetraethylammonium salts can make full claim to preparative use.

IV. SYNTHESIS OF COMPLEX GLYCEROPHOSPHATIDES

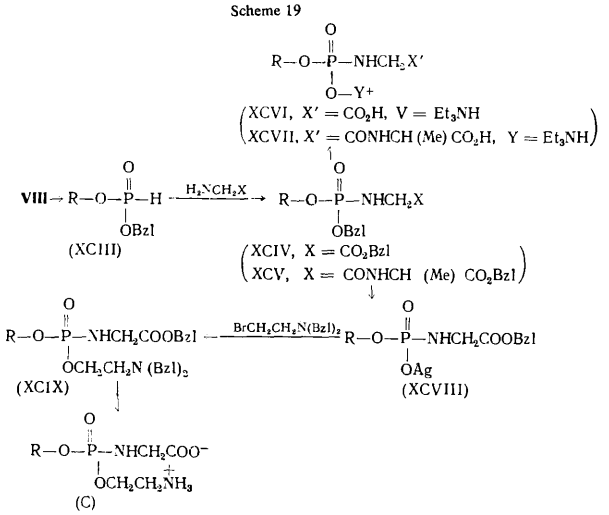
All the papers discussed have been concerned mainly with the synthesis of the so called classical diester glycerophosphatides. An exception is provided by the syntheses of amino-acid derivatives of certain phosphatides (XXXIII), (XXXIV), (XXXVI)–(XXXVIII), and (LIX)[69,70,73,90-92,105,157-161], phosphatidopeptides (XXXV), (LII), and (LIII),[16-21,67] the glucosamino-derivative of phosphatidylglycerol (LXIX),[22] and an *N*-glycoside of phosphatidylaminoethanol (LXXVII);[166] the need to discuss them in preceding Sections was dictated solely by methodological considerations. These compounds cannot be included among classical glycerophosphatides. Phosphatides which contain, besides the traditional structural units, amino-acids, peptides, carbohydrates, etc. are often termed complex phosphatides, and perhaps classical glycerophosphatides are fragments of these complex lipid structures, which are present in natural tissues and are easily decomposed in the course of isolation[193-199]. Another feature of these compounds is presumably a triester structure of the phosphate portion[193-199]. Progress in the synthesis of classical glycerophosphatides has enabled a close approach to be made to obtaining certain classes of complex phosphatides. The chief researches on these lines, other than the few discussed in the previous Sections, will be described below.

Among the most widely distributed complex phospholipids are amino-acid and peptide derivatives of glycerophosphatides. Besides the amino-acid derivatives of phosphatidylglycerol (XXXVII), (XXXVIII), and (LIX), phosphatidylpeptides based on cephalins and phosphatidylserines (XXXV), (LII), (LIII), and also cardiolipin[199] we may assume the possibility of the covalent addition of amino-acids and peptides to the phosphoric acid in glycerophosphatides by means of phosphoramide and acyl–phosphate bonds. Definite indications of the possibility of such complex formation have now been obtained[200].

1. Synthesis of Amino-acid and Peptide Derivatives of Phosphatidic Acid and Phosphatidylaminoethanol of Phosphoramide and Acyl Phosphate Types

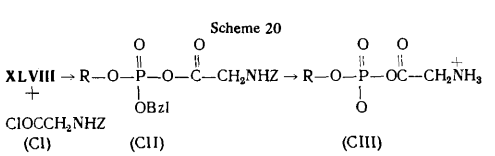
Phosphatidylamino-acids (XCVI)[24] and phosphatidylpeptides (XCVII)[24] containing a phosphoramido-bond are obtained (from 1,2-diglycerides) by a method widely used in the chemistry of nucleotide amino-acids and peptides[201] with synthetic procedures characteristic of glycerophosphatides. In order to obtain (P→N)-glycylphosphatidylaminoethanol (C) the corresponding protected derivative of phosphatidic acid (XCIV) is converted, by the methods described in Section II, into the silver salt (XCVIII), from which the cephalin (XCIX) is formed[26] (Scheme 19).

Scheme 19



A glycine derivative of phosphatidic acid of acyl phosphate type (CIII) is formed by reaction of silver benzyl phosphatidate (XLVIII) with *N*-benzyloxycarbonylglycyl chloride (CI) followed by removal of the protective groups (CII) → (CIII)[25] (Scheme 20).

Scheme 20

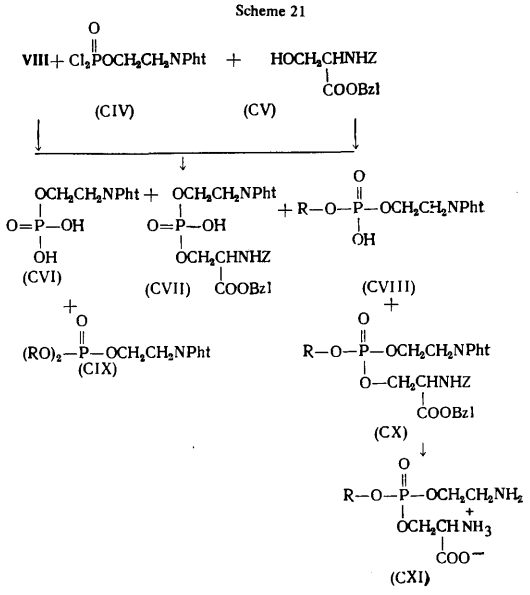


Investigations of the properties under comparable conditions of classical glycerophosphatides and of amino-acid and peptide derivatives of phosphatidic acid and phosphatidylaminoethanol—(XCVI), XCVII), (C), and (CIII)—have shown[24-26] the lower hydrolytic stability of the latter compounds. Both acyl–phosphatide and phosphoramide bonds are labile even in weakly acid media. Study of the structure and properties of the synthetic amino-acid and peptide derivatives of glycerophosphatides—(XCVI), (XCVII), (C), and (CIII)—suggests that such complex formation may occur in natural lipoproteins, but the exceptional lability of these structures creates serious difficulties in their isolation from natural sources in the native state, so that the question of the presence of compounds of this type in natural lipid–protein complexes is still a matter of controversy.

2. Synthesis of Triester Phosphatides and Phosphatidopeptides

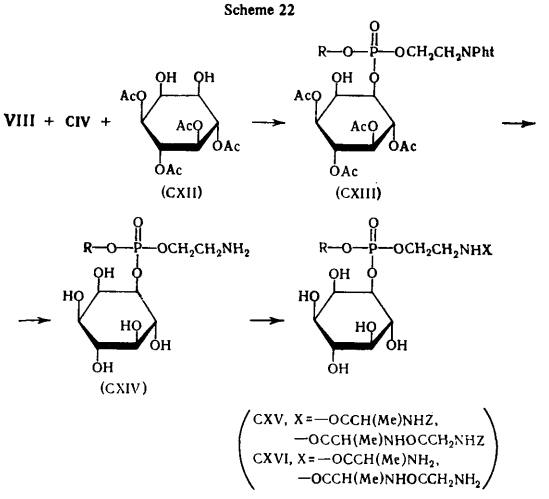
The preparation of triester phosphatides and phosphatidopeptides has been based on the method of synthesising diester glycerophosphatides from 1,2-diglycerides. Aminoethylphosphatidylserine (CXI)—a triester glycerophosphatide assumed to be present in the microsomes of brain tissue[202,203]—has been synthesised by reaction among the 1,2-diglyceride (VIII), 2-phthalimidoethyl phosphorodichloridate (CIV), and the dibenzyl ester of *N*-carboxyserine (CV), with subsequent removal of the protective groups (CX) → (CXI)[15] (Scheme 21). The course of the reaction is ambiguous, being accompanied by the formation of a series of phosphoric mono-, di-, and tri-esters (CVI)–(CIX), as a consequence of which the yield of aminoethylphosphatidylserine (CXI) after removal of the protective groups does not exceed 2–3%.

Scheme 21



The 1-*O*-aminoethylphosphatidylmyoinositol structure (CXIV) has been formed similarly[13]. The synthetic triester (CXIV) has been used to obtain phosphatidopeptides (CXVI)[16,21]—structural units in the lipid complex of ox brain[198]—by condensation of the amino-group in the aminoethyl residue of (CXIV) with the azides of *N*-benzyloxycarbonyl-alanine and -glycylalanine followed by removal of the protective groups by known methods (CXV) → (CXVI) (Scheme 22).

Scheme 22



Study of the stability of the synthetic triester phosphatides—(CXI), (CXIV), and (CXVI)—has shown that they are labile compared with the cephalins, phosphatidylserines, and phosphatidylinositols which they contain[13,15,16,21], this being fully consistent with published data[193-199] on the properties of triester phosphatides. The triester (CXIV) and (CXVI) containing myoinositol are considerably more stable than the triester (CXI),[13,15,16,21] which is supported by the assumed special role of myoinositol in the formation and functioning of complex phosphatides and phosphatidopeptides[198].

V. METHODS OF SYNTHESIS OF OPTICALLY ACTIVE PHOSPHOINOSITIDES

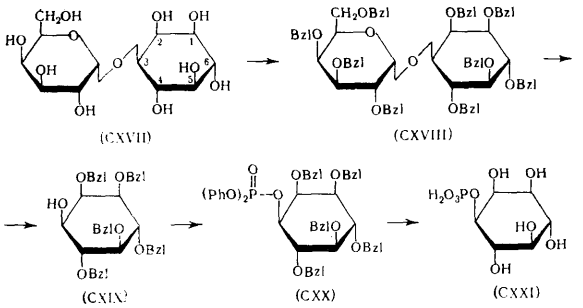
The problem of obtaining optically active phosphoinositides requires special consideration (all those mentioned hitherto were synthesised in optically inactive form). In naturally occurring phosphoinositides the myoinositol molecule is asymmetrically substituted in the 1-equatorial position by the phosphatidyl radical, and hence possesses optical activity. This has been proved both for inositophosphatides of simple structure[204-208] and for the complexes[209-212].

The problem of synthesising optically active phosphoinositides is in essence a particular case of the wider problem of obtaining optically active myoinositol derivatives. At the present time there are two approaches to a solution—(1) the use of natural substances (galactin, quebrachitol, bornesitol, etc.), in which molecular asymmetry is already established, for their further conversion into optically active asymmetrically substituted myoinositols of specified structure; and (2) the resolution of racemic asymmetrically substituted myoinositols, prepared from myoinositol itself, into enantiomers.

1. First Method

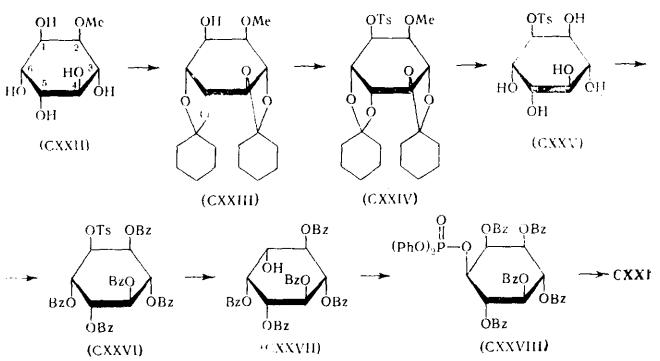
In 1959 Ballou reported[207] the synthesis of optically active *sn*-myoinositol 3-phosphate§. The starting material was galactin, which was completely benzylated (CXVII) → (CXVIII); methanolysis with 1% hydrochloric acid led to cleavage of the α-glycosidic bond in the nonabenzylgalactin (CXVIII); the resulting 1,2,4,5,6-penta-*O*-benzyl-*sn*-myoinositol (CXIX) was phosphorylated with diphenyl phosphorochloridate; and after removal of the protective groups *sn*-myoinositol 3-phosphate (CXXI) was isolated (Scheme 23).

Scheme 23



Gero[117] has recently proposed another route to the optically active 3-phosphate (CXXI), starting from quebrachitol (2-*O*-methyl-(−)-inositol) (CXXII). This was converted into 3,4 : 5,6-di-*O*-cyclohexylidenequebrachitol (CXXIII), which was then transformed into 3,4 : 5,6-di-*O*-cyclohexylidene-2-*O*-methyl-1-*O*-tosyl-(−)-inositol (CXXIV). The latter after elimination of the methyl group with boron trichloride gave 1-*O*-tosyl-(−)-inositol (CXXV). After benzoylation (CXXV) → (CXXVI) and removal of the tosyl group with inversion of the configuration of the 3-hydroxyl the product was 1,2,4,5,6-penta-*O*-benzoyl-*sn*-myoinositol (CXXVII), which was converted by the methods described by Ballou[207] into *sn*-myoinositol 3-phosphate (CXXI) (Scheme 24).

Scheme 24

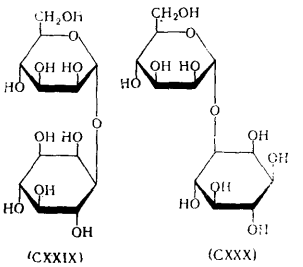


However, these syntheses[117,207,215] possess extremely serious limitations, and hence cannot be recommended for obtaining optically active phosphoinositides of natural structure. Apart from the difficult availability of galactin and quebrachitol, which are isolated from vegetable sources inaccessible in the Soviet Union, the many stages in the syntheses, and the low yields of optically active asymmetrically substituted myoinositols, a further significant defect must be mentioned. It is readily observed that the application of asymmetrically substituted myoinositols, obtained from galactin and quebrachitol, to the synthesis of optically active phosphoinositides will yield phosphatides containing the phosphatidyl group at the 3-position of myoinositol, i.e. of unnatural configuration.

The method of obtaining 2,3,4,5,6-penta-*O*-tosyl-*sn*-myoinositol from (−)-bornesitol (1-*O*-methyl-*sn*-myoinositol),[118,119] based on its exhaustive tosylation with subsequent removal of the methyl group with boron tribromide, does not possess this disadvantage. However, attempts to prepare phosphatidylinositol from 2,3,4,5,6-penta-*O*-tosyl-*sn*-myoinositol have encountered insuperable difficulties[118].

2. Second Method

Purely chemical methods for obtaining the two series of optically active derivatives of myoinositol have not been developed hitherto because of the great difficulty of resolving their racemic mixtures. Isolated papers have been published on unsuccessful attempts at separation[113]. Nevertheless, mention must be made of Angyal's work[216] on the preparation of mannosylmyoinositols, which were obtained in low (4.5%) yield by the Koenigs–Knorr reaction¶ and separated by crystallisation into two diastereomers—1- and 3-*O*-α-D-mannopyranosyl-*sn*-myoinositols



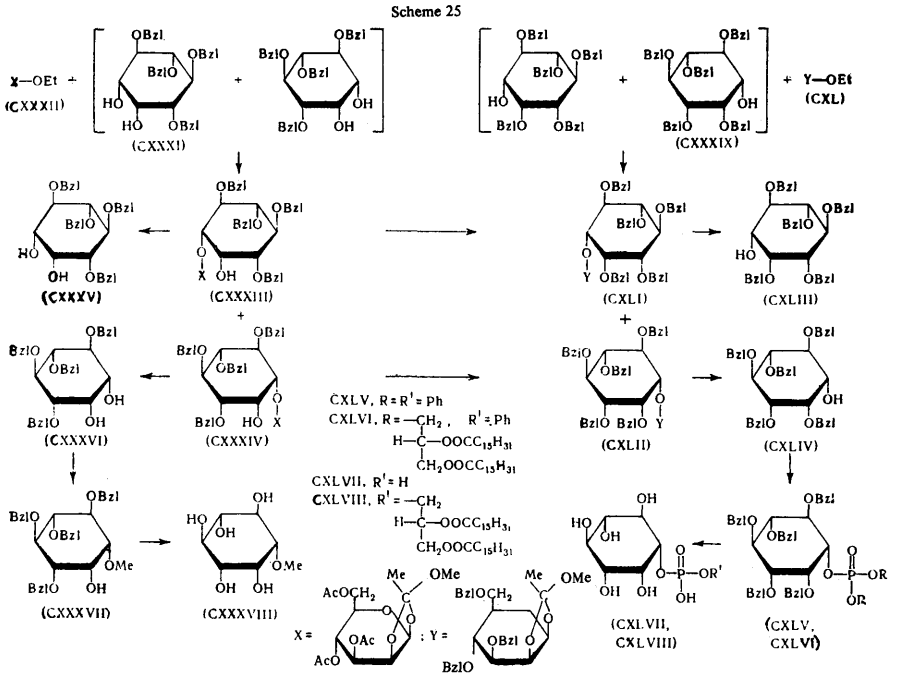
Use of the orthoester method of glycosylation[217] to form a glycosidic bond enabled the yield of diastereomeric mannosylmyoinositols (CXXIX) and (CXXX) to be raised considerably (to 10–12%).[218] The mannoside (CXXIX) might have served as initial compound for obtaining optically active 1-*O*-substituted derivatives of myoinositol, but this was prevented by its low yield in the main reaction.

A procedure has been developed recently in our laboratory for separating racemates of asymmetrically substituted myoinositols via the diastereomeric orthoacetates with D-mannose[219], which has opened a path to obtaining optically active phosphoinositides. Transesterification of 1,4,5,6-tetra-*O*-benzylmyoinositol (CXXXI) with D-mannose orthoacetate (CXXXII) gave the diastereomeric orthoesters (CXXXIII) and (CXXXIV), which were separated by crystallisation or by chromatography. Acid hydrolysis of these orthoesters yielded 1,4,5,6- and 3,4,5,6-tetra-*O*-benzyl-*sn*-myoinositols (CXXXV) and (CXXXVI). The absolute configuration of these products was established by conversion of (CXXXVI) into the methyl ether (CXXXVIII), which was compared with specimens of (+)- and (−)-bornesitols[220] (Scheme 25).

§ Our proposed nomenclature[213,214] is used for optically active myoinositol derivatives.

¶ The Koenigs–Knorr reaction has been used also to prepare galactin in 2.1% yield. In this case the diastereomers were separated by seeding with crystalline natural galactin[216].

Scheme 25



An attempt to use 3,4,5,6-tetra-*O*-benzyl-*sn*-myoinositol (CXXXVI) to synthesise the monophosphoinositide was unsuccessful owing to the presence of vicinal hydroxy-groups in (CXXXVI), which made it necessary to seek ways of synthesising the corresponding pentabenzyl derivatives. 2,3,4,5,6-Penta-*O*-benzyl-*sn*-myoinositol (CXLIV) was obtained from 1,2,4,5,6-penta-*O*-benzylmyoinositol (CXXXIX)[111,113,221] by the method developed for separating 1,4,5,6-tetra-*O*-benzylmyoinositol (CXXXI)[221] (Scheme 25).

Since the orthoesters (CXLI) and (CXLII) have very similar physicochemical properties and are therefore difficult to separate, the synthesis of the pentabenzyl ethers (CXLIII) and (CXLIV) was modified[222]. The orthoesters (CXXXIII) and (CXXXIV), easily obtained by the transesterification of 1,4,5,6-tetra-*O*-benzylmyoinositol (CXXXI),[220] were taken as starting materials. In this case formation of the orthoacetate with D-mannose was used both the resolve racemic compounds and to protect temporarily the 1- and 3-hydroxyls in myoinositol. The stability of the orthoester grouping under alkaline conditions was exploited by exhaustively benzylating (CXXXIII) and (CXXXIV) to (CXLI) and (CXLII), and hydrolysing in the usual way to the pentabenzyl ethers (CXLIII) and (CXLIV). Application of the new carbohydrate orthoester protection enabled optically active pentabenzyl ethers of myoinositol to be obtained in preparative quantities (Scheme 25).

2,3,4,5,6-Penta-*O*-benzyl-*sn*-myoinositol (CXLIV) has been used as starting material for the directed synthesis (Scheme 25) of the structural unit of all phosphoinositides—*sn*-myoinositol 1-phosphate (CXLVII)[221]—which proves to be identical with the *sn*-myoinositol 1-phosphate isolated from soya-bean phosphatides[207].

These investigations culminated in the first chemical synthesis of an optically active phosphatidylinositol[222,223] (Scheme 25). To obtain the monophosphoinositide (CXLVIII) the pentabenzyl ether (CXLIV) was condensed with 1,2-dipalmitoyl-*sn*-glycerol and phenyl phosphorodichloridate to give a compound (CXLVI) which on hydrogenation yielded phosphatidylinositol (CXLVIII). The properties of the synthetic phosphatidylinositol (CXLVIII) were closely similar to those of monophosphoinositides isolated from various natural sources[224,225].

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During preparation of the manuscript for press several papers have been published on the synthesis of glycerophosphatides and their structural units.

A new method has been developed for the synthesis of 1,2-diacyl-*sn*-glycerols from *sn*-glycerol 1,2-carbonate[226,227], obtained by a shorter route than the existing method[34] from 3,4-*O*-isopropylidene-D-mannitol. The preparation of 1,2-diglycerides by the direct esterification of this last compound[59], which was unsuitable for compounds containing higher aliphatic acid radicals, has been freed from this defect[228].

The natural glycolipids[229]—mannosyl and glucosyl diglycerides[230]—have been synthesised from the diglycerides obtained[226-228]. Galactosyldiglycerides have been prepared from 2,5-*O*-methylene-D-mannitol[231]. This same compound has been the starting material for a new synthesis of 1,2-diacyl-*sn*-glycerols undertaken in our laboratory, by means of which saturated and unsaturated 1,2-glycerides containing the same and different acid radicals can be obtained.

No fundamentally new work on the synthesis of nitrogen-containing glycerophosphatides has appeared recently, although several papers make a definite contribution to the further development of synthetic methods. Thus the use of 2,4,6-tri-isopropylbenzenesulphonyl chloride as condensing agent to produce a phosphoric ester bond[108] has been extended to the phosphatidyl derivative of L-threonine[232], this synthesis comprising initially the formation of the glycerophosphoric structure and then introduction of ester radicals by means of Lapidot's method using aliphatic acid anhydrides[189].

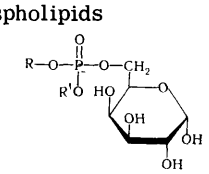
Several papers have appeared on the direct acylation of 3-*sn*-glycerylphosphorylcholine. Thus the cadmium complex of the 1-substituted compound has been used for exhaustive esterification of the 2-position with ^{14}C-labelled oleic acid[233]. Aneja and Chadha[234] have investigated the

mechanism of the esterification of 3-*sn*-glycerylphosphorylcholine by higher aliphatic acid chlorides. The formation of lecithin is shown to be accompanied by that of several more polar secondary products, which has a considerable effect on the overall yield of lecithin[6]. One of them is lysolecithin, and another—previously regarded as a cyclic lysolecithin[6]—is a mixture of isomeric monoacyldeoxychloroglycerylphosphorylcholines, the secondary products being formed from a common intermediate compound.

Among methodological papers mention must be made of the development of the mild removal, by means of zinc in acetic acid, of the phthalimidomethyl group[235], which is widely used for blocking the carboxyl function of amino-acids in the synthesis of phosphatidylserines and phosphatidylhydroxyprolines[81,87,92].

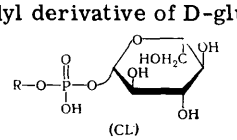
A series of syntheses of certain modified glycerophosphatides was designed to prepare materials for the investigation of enzymatic reactions with phosphatides, the part they play in the formation of biological membranes, etc. Thus, for the purpose of studying lipid–protein interactions by means of electron spin resonance spectroscopy in the investigation of lipolytic enzymes, *O*-(1,2-distearoyl-*sn*-glycerol-3-phosphoryl)-3′-oxymethyl-2′,2′,5′,5′-tetramethylpyrrolidine 1′-oxide has been synthesised by reaction between the corresponding phosphatidic acid and 3-hydroxymethyl-2,2,5,5-tetramethylpyrrolidine 1-oxide in the presence of 2,4,6-tri-isopropylbenzenesulphonyl chloride[236]. 3-Palmitoyl-*sn*-glyceryl-1-phosphorylcholine (lysolecithin of unnatural structure)[237] and also 2,3,4,5-tetrastearoyl-1,6-diphosphorylcholine-D-mannitol (an analogue of lecithin of unnatural structure)[238] have been prepared from 3,4-*O*-isopropylidene-D-mannitol and D-mannitol itself by methods which leave much to be desired from the viewpoint of the present-day chemistry of the glycerophosphatides. The glycerophosphatides obtained were investigated as substrates for phospholipases and acyltransferases. Similar methods have been used to obtain analogues of lysolecithins based on trimethylene glycol[239], which have been examined as components of artificial membranes.

Several papers deal with the synthesis of new glycerophosphatides. Thus the method of silver salts has been used for diester and triester glycophospholipids, which are assumed to be present in natural sources[196–198]. The synthetic glycophospholipids



(CXLIX, R′ = H, $CH_2CH_2NH_2$)

contain D-galactose attached by an ester link to the phosphatidyl group[240,241]. The same method has been used to obtain a phosphatidyl derivative of D-glucose



(CL)

but in this case the phosphatidyl group is attached at the anomeric hydroxyl (CL).[242]

In the field of the synthesis of phosphoinositides the resolution has been accomplished of racemic 1,2:5,6-di-*O*-cyclohexylidenemyoinositol[243], and each of the enantiomers—of 1,2:5,6- and 2,3:4,5-di-*O*-cyclohexylidene-*sn*-myoinositols—can be used as principal starting material for obtaining di- and tri-phosphoinositides and also other members of this class of phosphatides. Attempts to separate 1,2:4,5-di-*O*-cyclohexylidenemyoinositol into enantiomers[244], and also to use D-glucose orthoacetate instead of D-mannose orthoacetate for the resolution[244], have been unsuccessful.

Molotkovskii[245] has accomplished the synthesis of racemic phosphatidylinositol with unsaturated acids using 1,2,4,5,6-penta-*O*-acetylmyoinositol as inositol component. A phosphoric diester bond was formed by reaction of the 1,2-diacyl-3-deoxy-3-iodoglycerol with silver benzyl 1,2,4,5,6-penta-*O*-acetylmyoinositol phosphate.

Gigg and his coworkers[246] have examined in detail the possibility of producing a racemic phosphatidylinositol structure using—(1) the reaction of a 1,2-diacyl-3-deoxy-3-iodoglycerol with various silver phosphates containing 1,2,4,5,6-penta-*O*-benzylmyoinositol attached by a phosphoric ester bond, with subsequent removal of the protective groups by hydrogenolysis and anionic debenzylation; and (2) the reaction of 2,3,4,5,6-penta-*O*-benzylmyoinositol 1-phosphate (obtained by phosphorylation of the corresponding penta-substituted myoinositol with bis-2,2,2-trichloroethyl phosphorochloridate, the protective groups being removed with zinc dust in methanol) with a 1,2-diglyceride in the presence of 2,4,6-tri-isopropylbenzenesulphonyl chloride. The latter method is shown to have considerable advantages over the former.

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The Faraday Effect in Transparent Regions—An Unusual Method for the Investigation of Molecular Structures

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I. INTRODUCTION

Although 125 years have elapsed since the discovery by Faraday[1] in 1845 of the phenomenon of the rotation of the plane of polarisation in a magnetic field and although numerous investigators both in France and abroad devoted their lives to a profound study of this phenomenon and its applications in structural chemistry, in 1970 the Faraday effect is quite unfamiliar to chemists as a research technique.

The literature, which includes more than 200 papers, clearly shows that a powerful technique now exists whereby it is possible to solve, sometimes very successfully, a large number of problems in structural chemistry. Numerous meetings with investigators from different countries at conferences have revealed a considerable interest in this method. The question thus arises why the Faraday effect is known only to a limited circle of specialists while NMR, infrared, and ultraviolet spectroscopic techniques have become common and classical procedures. The answer is probably that all the papers describing the principles of the method and its applications have been published in French and, with rare exceptions, in French periodicals. It is therefore an urgent necessity to overcome the language barrier in order that the Faraday effect may become internationally known. Our attempt to solve this difficult problem was stimulated by the invaluable support of many well known investigators such as C. A. Coulson, H. D. Ballhausen, C. K. Jorgensen, A. Julg, R. Daudel, A. Sladkov, and J. R. van Wazer, to whom we are indebted for their assistance and advice in the compilation of this review.

II. WHAT IS THE FARADAY EFFECT?

As early as 1845, Faraday[1] made the following fundamental discovery: any transparent substance placed in a magnetic field H rotates the plane of polarisation when monochromatic light is passed through it. This phenomenon may be called magnetic rotation by analogy with natural rotation, although molecular asymmetry is evidently important for the latter, while the former is shown by any substance in a magnetic field. Faraday's experiments were repeated and extended by Becquerel[2], Mathiessen[3], and especially Verdet[4], who was the first to find a quantitative expression for the effect in the form

$$\alpha = \rho \int_0^l \boldsymbol{H} d\boldsymbol{l},$$

where l is the optical pathlength in the test substance and ρ a characteristic constant for the substance, which has been called the Verdet constant. Thus measurement of the angle α permits in principle the determination of the Verdet constants of the relevant compounds and also the corresponding molecular magnetic rotation $(\rho)_M$, defined by the expression

$$(\rho)_M = \frac{\rho}{d} \cdot M,$$

where M and d are the molecular weight and specific gravity of the substance.

This in broad outline is the observed phenomenon and about a century elapsed since its discovery before the following two fundamental questions were formulated:

1. What is the reason for the rotation of the plane of polarisation?
2. Is the Verdet's formula rigorously valid?

The answer to the first question in terms of classical quantum mechanics has been given in publications which are virtually inaccessible to physical chemists without sufficient experience in quantum-chemical calculations. Indeed the theoretical aspect of the magnetic rotation of the plane of polarisation (the electromagnetic wave, the magnetic field, and the set of molecular orbitals in the strong interaction condition) is so complex that, listening to lectures by theoretical physicists developing the formal mathematical side of the problem, one might sometimes ask whether the effect under discussion is indeed the one first observed by Faraday. To see this, it is sufficient to read only a few pages in papers by Kronig[5], Rozenfeld[6], Kramers[7], Groenewege[8], Smet[9-11], or I'Haya[12]. The concept which we shall now develop in a few words will undoubtedly arouse protests by theoreticians but it has the

advantage of a simple description of the basis of the phenomenon.

The presence of a magnetic field leads to complete loss of symmetry by molecular orbitals. If Ψ_0 denotes the wave function in the absence of the field, the perturbed wave function is

$$\psi = \psi_0 + \sum_k c_k \psi_k ,$$

where Ψ_k are the wave functions of the excited molecular states.

The change of Ψ_0 under the influence of the field H appears to involve the mixing of the ground and excited molecular states. It has been shown[13] that in first-order perturbation theory

$$c_k = \frac{-aH \int \psi_0 \frac{\partial}{\partial \theta} \psi_k d\tau}{E_0 - E_k} ,$$

where θ is the polar angle reckoned from the direction of H and E_0 and E_k are the energies of the levels corresponding to Ψ_0 and Ψ_k. It is immediately clear that the contribution by Ψ_k to perturbation will be non-zero only when Ψ_k includes symmetry elements antisymmetric to Ψ_0. This is in fact why, when Ψ_0 is the $2p_z$ orbital, only the $3d_{xy}$ orbital makes an appreciable contribution to the deformation of Ψ_0 and, when Ψ_0 is an s orbital, no orbital with an energy lower than that of the $4f$ orbital can be involved in the perturbation. As a result, one may say *a priori* that the Faraday effect due to the π electrons in the molecule is much greater than that due to the σ electrons, since $E_{2p_z} - E_{3d_{xy}}$ is always much smaller than $E_s - E_{4f}$. Subsequently we shall see that this is in fact so. Thus in a magnetic field molecular orbitals completely lose their symmetry and this is the reason for the optical anisotropy and the further consequences are fully analogous to those in the natural rotation of the plane of polarisation[14].

The second question posed above is no less important: one can show that the rotation α is not in fact strictly proportional to H but is expressed by a limited series

$$\alpha = aH + bH^2 + cH^3 + \ldots$$

Usually the "double rotation 2α", i.e. the sum of the rotations $+\alpha$ and $-\alpha$ observed for two opposite values of the field $+H$ and $-H$ is measured experimentally. This procedure eliminates terms proportional to the even powers of H in the expression for α. Therefore, if cH^3 is negligibly small, then $\alpha \propto H$, in agreement with Verdet. Detailed calculation of the quantities a and c shows that this is true, provided that H does not exceed 2.5×10^4 gauss. This limits has not so far been attained in classical apparatus for the measurement of the Faraday effect in the transparency range; the most powerful of these, which we have in our laboratory, has $H_{max} = 1.5 \times 10^4$ gauss. However, one must recognise that an increase of H_{max}, which might nowadays be expected by specialists in the field of the Faraday effect, would face the boldest investigators with the difficulties of non-linear quantum electrodynamics; their results could not be compared directly with the data of their colleagues, who, unable to use the new facilities for practical reasons, would continue to work in the region where α is fairly exactly proportional to H. This is indeed the case, but, having made these philosophical remarks, we shall now turn to the actual experimental technique and the results which it can yield.

III. EXPERIMENTAL ARRANGEMENT AND ACCURACY OF MEASUREMENTS

The optical system consists of a mercury lamp S emitting a characteristic spectrum from which the required line may be isolated by a monochromator M of TREGOR type. The monochromatic light beam passes through a polariser P and then through a polarimetric cuvette C in the gap of the electromagnet (Fig. 1). The rotation of the plane of polarisation is read off to within 0.01° with the aid of a Lippich polarimeter. The electromagnet is supplied with currents up to 200 A stabilised to within 1%, from a 150 V supply. The maximum magnetic field strength in the centre of the gap is of the order of 1.5×10^4 gauss for a homogeneity of 10^{-5} gauss cm^{-1} and a gap of 7 cm wide. The polarimetric cuvette, with an average length of 3 cm and a working volume of 2 cm^3, is thermostatted and located in the gap by means of adjustable brass holders clamped to the yoke of the electromagnet.

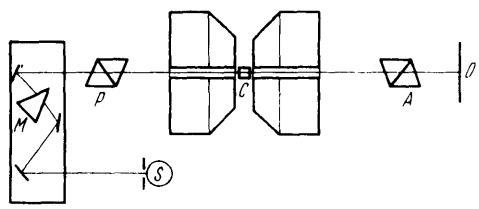


Figure 1.

The polarimetric readings can be made with two opposite directions of H and the resulting "double rotations 2α" reach on average 75°. To obviate the necessity for an accurate determination of the magnetic field gradient along the cuvette, relative measurements are usually made. If we denote by subscripts e and i the standard and test substances respectively, then

$$\frac{\alpha_i}{\alpha_e} = \frac{\rho_i}{\rho_e}$$

or, introducing the specific rotatory power (ρ_i) and the molecular rotatory power $(\rho_i)_M$:

$$(\rho_i)_M = \frac{\rho_e}{\alpha_e} \alpha_i \frac{M_i}{d_i} ,$$

where M and d denote the molecular weight and the specific gravity of the test substance. Doubly distilled water is used as a classical reference standard, since its Verdet constant at 20°C and a wavelength of 546 nm (the green line in the discharge spectrum of mercury) has been measured with a high accuracy by de Mallemann et al.[15] as 4.482 μrad (microradians). It was established that the magnetic rotation of the substance depends on the wavelength at which the measurements are made[16], on temperature[17,18], and on the physical state of the test substance[19]. As regards the first factor, it is assumed that the substance exhibits *normal dispersion*, provided that the measured Verdet constants at $\lambda_1 = 578$ nm, $\lambda_2 = 546$ nm, and $\lambda_3 = 436$ nm satisfy the relations

$$\frac{\rho(\lambda_3)}{\rho(\lambda_1)} = 1.86 \text{ and } \frac{\rho(\lambda_2)}{\rho(\lambda_1)} = 1.13 .$$

The dispersion for covalent and diamagnetic molecules and molecules without transition elements is always normal as long as the first vertical transition for these compounds in the ultraviolet region lies below 280 nm.

The effect of temperature and the physical state on the magnetic rotation of a given substance has been the subject of numerous investigations. In particular, de Mallemann established that

$$(\Omega)_M = \frac{9n}{(n^2+2)^2}(v)_M$$

is an invariant quantity for all changes [in the system]. In this formula n is the refractive index at the experimental wavelength and temperature[19]. Recently Dagnac-Amans[20] showed that molecular magnetic rotation can always be used over a wide temperature range centres on 20°C for a satisfactory description of the magneto-optical properties of a single molecule. She also succeeded in showing, having confirmed the individual results of the work of Dupouy and Fert[17], that magnetic rotation decreases slightly (and linearly) with increasing temperature (except for H_2O and D_2O). Table 1 lists specific data confirming this finding.

Table 1.

CS_2	$y=-0.658\ t+781.6$	$CH_3(CH_2)_2CH_2OH$	$y=-0.024\ t+342.0$
C_6H_6	$y=-0.216\ t+811.8$	CH_3COCH_3	$y=-0.024\ t+249.3$
CCl_4	$y=-0.073\ t+472.0$	CH_3OCH_3	$y=-0.020\ t+191.7$
$CH_3CH_2CH_3$	$y=-0.071\ t+258.0$	D_2O	$y=+0.012\ t+77.8$
SO_2	$y=-0.066\ t+219.5$	H_2O	$y=+0.006\ t+71.6$

On our apparatus, it is possible to investigate either liquids in the temperature range between −120° and +120°C or solutions of sparingly soluble substances in a suitable solvent. The optical measurements do not present any difficulties in the first case and one can be certain that the accuracy attained in the measurement of molecular rotation is about 0.3%. In the second case fundamental difficulties arise because of the importance of the choice of solvent. Initially one must make sure that in the test solution there are no chemical or physical interactions between the solute and solvent and that one may employ the relations established by Verdet[4] for ideal mixtures, according to which each component makes an additive contribution to the overall magnetic rotation. Then it is necessary to select a solvent whose Verdet constant differs sufficiently from the analogous constant of the test solution. This factor, which is very sensitive in practice, must be satisfied with great precision, since it determines the success of the measurements. In view of all these considerations, measurements in solutions must be resorted to only in extreme cases and the accuracy of the molecular rotation thus obtained does not exceed 1%. In an attempt to obviate this difficulty, Zarzycki and Naudin[21] devised a special apparatus permitting observations on compounds in the liquid state, whose melting points may reach 1100°C.

After this brief description of the classical experimental arrangement, we proceed to the review of the fundamental applications of the method in studies on problems in structural chemistry, which are of the most immediate interest.

IV. THE FARADAY EFFECT AND THE ADDITIVE PROPERTIES OF MATTER

We have just seen how magnetic molecular rotation (a generalised property) characterising the test substance may be determined by a simple polarimetric measurement, provided that the specific gravity is known. Because of this generality, non-specialists believed for a long time that the Faraday effect constitutes a less powerful method than NMR or infrared spectroscopy, since the latter make it possible, in principle, to determine the essential characteristics of the nucleus or a given bond. We shall now see that in fact such discrimination is invalid and is based solely on the ignorance of the magneto-optical phenomenon. Magnetic rotation of polarisation is an additive property of matter: the question arises of the significance of this assertion and its basis. All the experimental data accumulated during the period since the Faraday effect has been known indicate a systematic additivity of magnetic rotation, similar to that discovered by Pascal and coworkers[22] in diamagnetism, which frequently makes it possible to calculate with surprising accuracy the molecular rotation of a compound, provided that two conditions are satisfied: (1) only covalent, normal, diamagnetic, σ, or π localised bonds are present; (2) the bond constant has been explicitly defined.

In 1960 Gallais and Voigt[23] first suggested that additivity may be expected for magnetic rotation per bond. The difficulty of determining the magnetic rotation parameters referred to individual bonds consists in the necessity of separating a generalised quantity for the atom into components characterising individual bonds in such a way that each bond constant is independent of the individual characteristics of the others. Moreover, the quantity characteristic of the atom as a whole must evidently be the same every time. This problem hardly exists in organic chemistry, since carbon almost always exhibits the same coordination and employs four valence electrons. However, it is important for inorganic chemistry, where atoms can have significantly different coordinations. In order to overcome this difficulty, it is necessary (1) to define bond constants in such a way that they are independent of the coordination of the atoms involved in the given bond and (2) account must be taken of the behaviour of lone electron pairs not involved in any interatomic bond.

The first conditions may be satisfied simply by dividing the generalised quantity characterising the atom into equal parts among the n_E valence electrons, assuming that they are all equally active as regards the optical, magnetic, and magneto-optical properties. The modulus α (for refraction, magnetisation, and magnetic rotation) of a single σ or π bond between two atoms A and B is then uniformly represented by the symbol

$$\alpha\left(\frac{A}{n_A}-\frac{B}{n_B}\right)$$

and if the atom X contributes two electrons to the bond (a double bond, or a donor–acceptor bond in which X is an electron-donating atom), its contribution to a bond of this kind becomes $2X/n_X$, etc.

Tables 2–4 present data on the magnetic rotation due to the commonest bonds, determined in accordance with the above principles from chemical data for carbon[23,24], boron[25-30], aluminium[31,32], gallium[33], nitrogen[23,34], sulphur[20,35], and phosphorus[36,37]. Having at one's disposal the required set of bond constants, it is easy to calculate the magnetic rotation, provided that, taking into account Eqn. (2), the contribution $\alpha(e)$ by lone electron

Table 2.

Bond	ρ, μrad	Bond	ρ, μrad
$\left(\frac{C}{4}-\frac{C}{4}\right)_{\sigma}$	18.50	$\left(\frac{C}{4}-\frac{N}{3}\right)$: (NR_3)	47.0
$\left(\frac{C}{4}-\frac{C}{4}\right)_{\pi}$: $(H_2C=CH_2)$	117	$\left(\frac{3C}{4}\equiv\frac{N}{1}\right)_{\sigma+\pi}$: nitriles	65.5
$\left(\frac{C}{4}-\frac{C}{4}\right)_{\pi}$: $(HC\equiv CH)$	77.5	$\left(\frac{C}{1}\equiv\frac{2N}{3}\right)_{\sigma+\pi}$: isonitriles	119
$\left(\frac{C}{2}=\frac{C}{2}\right)_{\sigma+\pi}$	135	$\left(\frac{C}{4}-\frac{Si}{4}\right)$	74
$\left(\frac{3C}{4}\equiv\frac{3C}{4}\right)_{\sigma+\pi}$	173	$\left(\frac{C}{4}-\frac{Ge}{4}\right)$	101
$\left(\frac{C}{4}-H\right)$	27.25	$\left(\frac{C}{4}-\frac{Sn}{4}\right)$	174
$\left(\frac{C}{4}-F\right)$	20	$\left(\frac{C}{4}-\frac{Pb}{4}\right)$	278
$\left(\frac{C}{4}-Cl\right)$	131	$\left(\frac{C}{4}-\frac{Be}{2}\right)$	190
$\left(\frac{C}{4}-Br\right)$	267	$\left(\frac{C}{4}-\frac{Hg}{2}\right)$	260
$\left(\frac{C}{4}-I\right)$	566	$\left(\frac{Si}{4}-\frac{O}{2}\right)$: $(Si(OR)_4)$	28.9
$\left(\frac{C}{4}-\frac{O}{2}\right)$	14.2	$\left(\frac{Si}{4}-Cl\right)$: $(SiCl_4)$	171
$\left(\frac{C}{2}=\frac{O}{1}\right)_{\sigma+\pi}$: acid	30.6	$\left(\frac{Si}{4}-\frac{Si}{4}\right)$: (Si_2R_6)	325
$\left(\frac{C}{2}=\frac{O}{1}\right)_{\sigma+\pi}$: aldehydes	35.5	$\left(\frac{N}{3}-H\right)$: (R_2NH)	20
$\left(\frac{C}{2}=\frac{O}{1}\right)_{\sigma+\pi}$: ketones	41.7	$\left(\frac{O}{2}-H\right)$: $(R\cdot OH;\ R\cdot CO_2H)$	28.0
$\left(\frac{C}{4}-\frac{S}{2}\right)$	126	$\left(\frac{S}{2}-H\right)$: (RSH)	158
$\left(\frac{C}{2}=\frac{S}{1}\right)_{\sigma+\pi}$: (CS_2)	385		

Table 3.

Bond	ρ, μrad	Bond	ρ, μrad
$\left(\frac{B}{3}-\frac{C}{4}\right)$	45	$\left(\frac{B}{3}-H\right)$	—
$\left(\frac{B}{3}-\frac{O}{2}\right)$	18	$\left(\frac{B}{3}-\frac{B}{3}\right)$	51
$\left(\frac{B}{3}-\frac{S}{2}\right)$	140	$\left(\frac{Al}{3}-\frac{C}{4}\right)$	138
$\left(\frac{B}{3}-\frac{Cl}{1}\right)$	145	$\left(\frac{Ga}{3}-\frac{C}{4}\right)$	165
$\left(\frac{B}{3}-\frac{Br}{1}\right)$	300	$\left(\frac{In}{3}-\frac{C}{4}\right)$	307

pairs is added. This condition is so important that its neglect immediately leads to considerable errors: unfortunately, in most studies on molecular interaction and almost always in the field of dipole moments, the contribution by lone electron pairs of atoms in the molecule is disregarded in the calculation of molecular quantities. Soon we shall see that the magnetic rotation which may be attributed to lone electron pairs is usually very considerable. There exists a simple method of estimating their contribution to a first approximation: it was used for the first time in the field of molecular refraction by Le Fevre and coworkers[38] at the time when we were preparing to publish analogous reports on the Faraday effect[39]. For this purpose, one must consider the changes in the magnetic rotation $\rho(C-E)$ due to the carbon–element bond as a function of the position of E in the Periodic System.

Table 4.

Bond	ρ, μrad	Bond	ρ, μrad
$\left(\frac{P}{3}-\frac{C}{4}\right)$	159	$\left(\frac{S}{2}-\frac{C}{4}\right)$	126
$\left(\frac{P}{3}-\frac{O}{2}\right)$	110	$\left(\frac{S}{2}-\frac{O}{2}\right)$	105
$\left(\frac{P}{3}-\frac{S}{2}\right)$	364	$\left(\frac{S}{2}-\frac{Cl}{1}\right)$	286
$\left(\frac{P}{3}-\frac{Cl}{1}\right)$	262	$\left(\frac{S}{2}-H\right)$	158
$\left(\frac{P}{3}-\frac{Br}{1}\right)$	550	$\left(\frac{S}{2}-\frac{S}{2}\right)$ (RS—SR)	319
$\left(\frac{P}{3}-\frac{P}{3}\right)$ (R_2P-PR_2)	349	$\left(\frac{Se}{2}-\frac{C}{4}\right)$	200
$\left(\frac{As}{3}-\frac{C}{4}\right)$	190	$\left(\frac{Se}{2}-H\right)$	250
$\left(\frac{As}{3}-\frac{O}{2}\right)$	150		

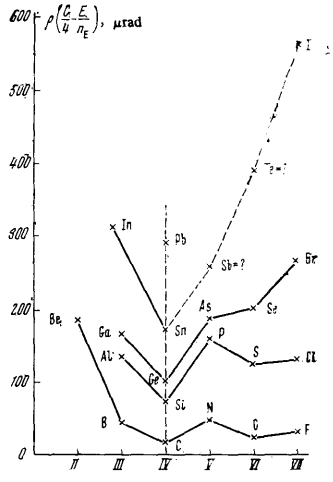


Figure 2.

Fig. 2 shows that the rotation increases rapidly within each Group, whereas in each horizontal Period it passes through a minimum when E belongs to Group IV. A detailed study of these changes leads to progress in the solution of the problem, which consists in the separation of the effects of various factors on the magnetic rotation due to the bond. Four factors may be regarded *a priori* as important: (1) the change in the overall value for the atom E involved in the bond $(C/4-E/n_E)$, while the analogous quantity for carbon remains constant; (2) proportionality to the amount

of ionic character of the bond; (3) the type of hybridisation of the atom E; (4) and, evidently, the activity of the corresponding lone electron pair of the atom E.

Simple considerations demonstrate that the third and fourth factors are dominant in the variation of $\rho(C-E)$. On the other hand, the decrease of the magnetic rotation due to the bond, on passing from Group II to IV, may be attributed only to the first and second factors and the minimum in the observations when E belongs to Group IV must be caused by the simultaneous operation of the first and second factors, the second predominating. Analysis of the left-hand part of the plot in Fig. 2 shows how $\rho(C-E)$ changes as a function of the hybridisation of the atom E. On passing from Group II to Groups III and IV, the fraction of s character of the atomic orbitals involved in the bond increases from 50 to 75 (in accordance with the change in hybridisation: $sp-sp^2-sp^3$). One must assume that the s character of the atomic orbitals of E and the rotation due to the (C–E) bond vary in parallel. Thus we arrive at the hypothesis, put forward by Le Fevre and coworkers[38] and Gillis[40] to account for the decrease of the (C–E) bond refraction in the given case. However, contrary to the postulates of these investigators, there is no doubt that the fraction of s character of the bond and refraction or rotation are not linearly related. Admittedly, in any type of linear relation between $\rho(C-E)$ and the amount of s character there should be no change in $\rho(C-E)$ on passing to Groups V, VI, and VII, since the hybridisation of nitrogen atoms in NH_3, of oxygen atoms in OR_2, and of fluorine atoms in FR remains close to sp^3. The increase of $\rho(C-E)$ actually observed appears to be caused, under these conditions, by the contribution from the lone electron pairs of the atom E, which may be calculated using the definition of bond rotation and the symbolism of the systematic additive scheme. Thus for phosphorus (a Group V element), we have

$$\rho\left(\frac{C}{4}-\frac{P}{3}\right)=\rho\left(\frac{C}{4}-\frac{P}{5}\right)+\frac{1}{3}\rho(d_P)=\rho^*(C-P)+\frac{1}{3}\rho(d_P),$$

and by hypothesis

$$\rho^*(C-P)=\rho\left(\frac{C}{4}-\frac{Si}{4}\right),$$

whence

$$\rho(d_P)\sim 3\left[\rho\left(\frac{C}{4}-\frac{P}{3}\right)-\rho\left(\frac{C}{4}-\frac{Si}{4}\right)\right]\sim 225\ \mu\text{rad}.$$

Similarly, for a Group VI element,

$$\rho\left(\frac{C}{4}-\frac{S}{2}\right)=\rho\left(\frac{C}{4}-\frac{S}{6}\right)+\frac{1}{2}\rho(2d_S)=\rho^*(C-S)+\rho(d_S);$$

using

$$\rho^*(C-S)=\rho\left(\frac{C}{4}-\frac{Si}{4}\right);$$

we have

$$\rho(d_S)=\left[\rho\left(\frac{C}{4}-\frac{S}{2}\right)-\rho\left(\frac{C}{4}-\frac{Si}{4}\right)\right]\simeq 52\ \mu\text{rad},$$

and, finally, for a Group VII element, for example chlorine, we have

$$\rho\left(\frac{C}{4}-\frac{Cl}{1}\right)=\left[\rho\left(\frac{C}{4}-\frac{Cl}{7}\right)+\rho(3d_{Cl})\right]=\rho^*(C\text{—}Cl)+3\rho(d_{Cl}),$$

$$\rho(d_{Cl})=\frac{1}{3}\left[\rho\left(\frac{C}{4}-\frac{Cl}{1}\right)-\rho\left(\frac{C}{4}-\frac{Si}{4}\right)\right]=19\ \mu\text{rad}.$$

The contributions by the lone electron pairs calculated in this way are listed in Table 5. Evidently the magnetic rotation due to a lone electron pair is often very considerable (compared with the contribution by the bond electron pair) and is a maximum for Group V elements. This result is consistent with the well known fact that phosphorus is a more powerful electron donor than sulphur and SX_2 molecules are stronger Lewis bases than XCl. The previous conclusions are based to a significant extent on the occurrence of a systematic additivity (which has not yet been discussed) of the magnetic rotation due to bonds, provided that the latter are covalent, normal, diamagnetic, and localised. The experimental evidence for such systematic behaviour has quite recently received valuable theoretical support in a paper by Daudel, employing analysis based on the "cell" theory† [41–44]. Systematic additivity is confirmed with the aid of the cell concept provided that three criteria are satisfied[45].

1. There is a clear subdivision of molecular space into cells (the probability of the residence of a single electron within a specified sphere is close to unity).

2. The quantity A is the sum of the A_i which are in turn expressed thus:

$$A_i=\int_{E-L_i} dv_{p+1}\ \ldots\ dv_n \int_{L_i}\psi^* A_{op}\psi dv_1\ \ldots\ dv_p,$$

and $A=\Sigma A_i$ (it is assumed that the cell L_i contains p electrons).

Table 5.

Element	Group V	Group VI	Group VII
Element E	N	O	F
$\rho(D)_E$, μrad	86	(—4.3)	(+0.5)
Element E	P	S	Cl
$\rho(D)_E$, μrad	255	52	19
Element E	As	Se	Br
$\rho(D)_E$, μrad	267	103	55
Element E	—	—	I
$\rho(D)_E$, μrad	—	—	131

3. The values of A_i for a given type of cell vary little in the series of molecules investigated.

Criterion *2* is fundamental to the interpretation of Daudel et al.[45], who were able to show that magnetic rotation satisfies it and therefore the classification of the additive properties in the Faraday effect is justified[46,47].

Since this is so, subsequent solution of problems in structural chemistry on the following basis is permissible: *all structural features of compounds with covalent, diamagnetic, and localised σ and π bonds must be duly reflected to some degree in a deviation from the law of additivity*. However, before concluding the section of definitions, we feel it desirable to consider the deeper significance of the systematic scheme. Such a scheme is very useful to the experimenter, who can ascertain by simple addition the purity of a compound just obtained. However, in terms of ideas, one must be firmly convinced that the bond constant is a constant quantity regardless of the environment of the bond in the remaining part of the molecule. This is undoubtedly shocking to critical minds.

† See Daudel's book[185] (Editor) [the original French term is "loge" (Ed. of Translation)].

How is it possible for magnetic bond rotation to be invariant in a molecule, while all other properties (vibration frequencies, bond lengths, ionic character, etc.) change? This remark in fact led us in 1964 to make a closer examination of the implications of the systematic scheme.

We know that the magnetic polarisability of a σ bond depends primarily on the shape of its electron cloud. We believe that the simplest semiempirical parameter providing a description of this configuration should be the partial ionic character of the bond as defined by Pauling. If we wish to find a relation between the rotation ρ_{AB} of a covalent σ bond (A–B) and the amount of its ionic character I_{AB}, it is necessary to have at ones disposal a method for calculating the effective value of I_{AB} for various possible situations in the molecule. Ultimately we decided on an iterative method[48] based on the use of self-consistent Pauling exponential functions modified and extended to the molecules M(XYZ...). A formal description of this procedure was given by Daudel in 1946 for symmetrical molecules MX_n.[49] In this way we were able to compare the effective values of I_{AB} obtained for all bonds in any covalent compound with the experimental values of ρ_{AB} obtained for these series of compounds without needing to postulate the constancy of the modulus of bond rotation, which is now regarded as a function of I_{AB}.

Table 6.

Compound	I_{BC}	ρ_{BC}	I_{BCl}	ρ_{BCl}
BCl_3	—	—	12.2	143.4
BCl_2R	3.9	57.9	13.1	140.7
$BClR_2$	4.6	50.4	14.4	136.8
BR_3	5.1	45.0	—	—

This enabled us to demonstrate a linear relation between ρ_{AB} and I_{AB}, which is demonstrated in Table 6 for certain most common bonds of boron[50] and phosphorus[51]. We chose these examples from others, since subsequently the corresponding equations will prove useful. Examination of Table 6 shows in the first place that b_{AB} is in all cases negative: it is quite logical that a higher value of I_{AB} is associated with a greater shift of the electron cloud and its concentration at the more electronegative atom. On the other hand, its deformability under the influence of the magnetic field is weaker and consequently the Faraday effect associated with this bond is smaller. The numerical value of b_{AB} is equally interesting. For similar bonds of boron and phosphorus (B–C and P–C, B–O and P–O), the b_{AB} values are virtually identical, which must be attributed to the similarity of the electronegativities (1.9 and 2.1 on Gordy's scale[52]). We may note further that b_{AB} decreases and tends to zero when the difference between the electronegativities δ_X of the atoms A and B increases. The limit is virtually attained for the (B–O) and (P–O) bonds ($\delta_X = 1.5$), which suggests that any (A–B) bond with $\delta_X \geqslant 1.5$ will have $b_{AB} = 0$ and will therefore give rise to a constant magnetic rotation regardless of the molecule in which this bond is located. In particular, the (P–F) bond is of this type, provided of course it is a σ bond. As this is correct, there arises immediately the following valid question concerning all that has been said above: how to reconcile the experimental finding of a systematic additivity of the moduli (constants) and the existence, proved theoretically, of a linear variation of these constants as a function of I. It is simplest to analyse one example, which provides a perfectly clear illustration: Table 6 shows how the ionic character of the (B–C) and (B–Cl) bonds varies in the $BR_{3-x}Cl_x$ series; evidently in the mixed compound $BRCl_2$, I_{BC} and I_{BCl} are respectively smaller and bigger than the corresponding quantities in BR_3 and BCl_3. Since b_{BC} and b_{BCl} are negative, ρ(B–C) and ρ(B–Cl) will be respectively bigger and smaller than the values in BR_3 and BCl_3. Thus it is sufficient to show numerically, which is not difficult, that the two deviations cancel out, since the essential features of the systematic additivity with constant moduli again become evident (Table 7).

Table 7.

Bond	$\rho_{ij} = a_{ij} + b_{ij} I_{ij}$	Bond	$\rho_{ij} = a_{ij} + b_{il} I_{ij}$
B–O	$\rho = 32.6 - 0.7 \cdot I_{BO}$	P–O	$\rho = 110 - 0 \cdot I_{P-O}$
B–Cl	$\rho = 180 - 3 \cdot I_{BCl}$	P–Cl	$\rho = 294 - 3.3 \cdot I_{PCl}$
B–C	$\rho = 99.6 - 10.7 \cdot I_{BC}$	P–C	$\rho = 182.9 - 9.2 \cdot I_{PC}$

The systematic additivity is in fact due to the cancellation of the terms $b_{BA}I_{AB}$ within the molecule. Thus everything falls into place. We believe that this result is doubly valuable. Firstly, it shows that the existence of systematic additivity is not fortuitous and, in addition, it provides a simple interpretation of the existence of certain σ covalent molecules which do not obey systematic additivity no matter which property one attempts to treat as an additive function. We preferred not to discuss this in Section II, in order not to draw readers' attention to details, which might have made it difficult to assimilate the main ideas. However, the time has now come to deal with this question: it concerns essentially molecules of the type $CCl_{4-x}H_x$. As early as 1910, Pascal[53] noted their anomalous diamagnetic behaviour, while Gallais and Voigt somewhat later[23] arrived at a similar conclusion concerning the Faraday effect.

Evidently, there should be no intramolecular compensation in these molecules. This compensation occurs only if the electronegativity of the central atom M is outside the range of electronegativities of the substituents X and Y (and b_{MX} and b_{MY} are negative). Halogenomethanes do not exhibit additivity, since this condition does not hold for them and indeed

χ_H	χ_C	χ_{Cl}
2.10	2.55	2.97

The observations which have worried the specialists in the field of the additive properties of matter for many years can be explained similarly[50]. The additivity of the Faraday effect was discussed and demonstrated in such detail in order to employ the deviations from this law for the solution of specific problems in structural chemistry.

V. MAGNETO-OPTICAL INVESTIGATION OF CONJUGATION PHENOMENA

In 1960 we made a detailed study of additive properties in the presence of electrons delocalisation in the molecule. Our investigation concerned primarily conjugated aliphatic

systems (pure hydrocarbons). The results are presented in Table 8; we established that the presence of a delocalised π-electron system in open-chain molecules always leads to a considerable positive deviation from additivity[54]. This fundamental result implies that the experimental molecular rotation (A) of a conjugated compound is always higher than the theoretical value (B) which may be calculated by additivity on the assumption that the molecule contains only localised bonds. Thus the exaltation of magnetic rotation (E) due to conjugation (briefly, conjugation exaltation) proves in addition to be constant for a given conjugation fragment and, conversely, is appreciably different for different conjugation fragments (Table 8). Analogous results were obtained for a large number of conjugated aliphatic moieties incorporating (C=O) and (C=N) bonds[55-58].

Table 8.

Formula	A	B	E
$CH_2=CH-CH=CH_2$	570	453	+117
$CH_2=CH-CH=CH-CH_3$	632	514	+118
$CH_2=CH-CH=CH-C_2H_5$	716	599	+117
$CH_3-CH=CH-CH=CH-CH_3$	695	575	+120
$CH_3-CH=CH-CH=CH-C_2H_5$	779	660	+119
$CH_3-CH=CH-CH=CH-C_3H_7$	853	733	+120
Mean			+119
$CH_2=C(CH_3)-CH=CH_2$	632	514	+118
$CH_2=C(CH_3)-C(CH_3)=CH_2$	695	575	+120
$CH_3-CH=C(CH_3)-CH=CH_2$	705	576	+129
$(CH_3)_2C=CH-CH=CH_2$	700	576	+124
$(CH_3)_2C=CH-CH=CH-CH_3$	762	637	+125
Overall mean (from No.1 to 11)			+121
$CH_3-CH=C(CH_3)-C\equiv CH$	633	560	+73
$CH_3-CH=C(CH_3)-C\equiv C-CHOH-C_3H_7$	919	867	+52
$C_4H_9-C\equiv C-C(CH_3)=CH-CH_3$	916	852	+64
Mean			~+63
$C_2H_5-C\equiv C-C\equiv CH$	641	566	+75
$C_4H_9-C\equiv C-C\equiv CH$	791	712	+79
$C_2H_5-C\equiv C-C\equiv C-COH(CH_3)_2$	898	823	+75
$C_4H_9-C\equiv C-C\equiv C-COH(CH_3)_2$	1047	969	+78
Mean			+77
$C_4H_9-C\equiv C-C\equiv C-C(CH_3)=CH_2$	1080	982	+ 98
$CH_2=CH-CH=CH-C\equiv CH$	786	645	+141
$CH_2=CH-CH=CH-CH=CH_2$	873	662	+211
$C_3H_7-CH=C=CH_2$	572	560	+ 12
$C_4H_9-CH=C=CH_2$	643	633	+ 10
$C_6H_{13}-CH=C=CH_2$	791	779	+ 12
$CH_2=CH-CH=C=CH_2$	664	549	+115
$C_2H_5-CHOH-CH=C=CH-CH=CH-CH_3$	965	844	+121
$C_2H_5-COH(CH_3)-CH=C=CH-CH=CH_2$	985	872	+113
$CH_3-COH(CH_3)-CH=C=CH-CH=CH_2$	935	806	+129
Overall mean (from No.25 to 28)			+120

Since the existence of E is associated with the delocalisation of π electrons, it was logical to find if E depends in some simple manner on the parameters employed in theoretical chemistry to describe delocalisation. For this purpose, we calculated in terms of the Hückel approximation the π-electronic structures of all the molecules investigated. We obtained the bond indices p_{rs}, the charges q_r localised at the atoms, and the free valence indices I_r,[59-61] and concluded that the sum of the free valence indices is in fact the required parameter, since the E vary linearly with it, as shown by Table 9 and Fig. 3, the correlation coefficient obtained by least-squares treatment of the results exceeds 0.96.

We shall note immediately that there exist apparently two $E = f(\Sigma I_r)$, straight lines, one (D_1) referring to moieties incorporating only double and triple bonds and the other (D_2) describing mixed moieties.

Table 9.

P { >C=C< $E=0$ $\Sigma I_r=1.464$; —C≡C— $E=0$ $\Sigma I_r=1.464$

(D_1) straight line	E	ΣI_r	(D_2) straight line	E	ΣI_r
(α)—C≡C—C≡C—	+ 77	2.136	(D) >C=C—C≡C—	+ 63	2.494
(β)>C=C—C=C<	+121	2.509	(E)—C≡C—C≡C—C=C<	+ 98	2.926
(γ)>C=C—C=C—C=C<	+211	3.476	(F) >C=C—C=C—C≡C—	+141	3.574
(δ)N≡C—C≡C—C≡N	+ 40	1.836	(G)—C≡C—C=O	+ 12	1.882
(ε)—C≡C—C≡N	+ 40	1.840	(H)>C=C—C≡N	+ 40	2.093
(μ)>C=C—C=O	+ 44	1.843	(J)O=C—C≡C—C=O	+ 50	2.286

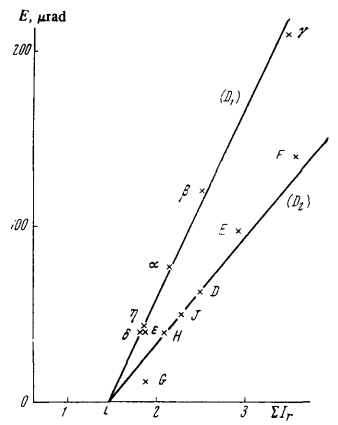


Figure 3.

This difficulty undoubtedly shows that the method of calculation employed (the Hückel approximation) does not allow a description of the second case with the same rigour as the first. In fact the calculation does not take into account a significant interaction between π-electron systems and the π-electron system of the triple bond, when it is conjugated with a double bond, which leads to low values of the bond indices and an appreciably high value of the sum of the free valence indices. Evidently, a more refined method of calculation would yield for compounds with mixed moieties a lower sum of the free valence indices compared with the values in Table 9, which would shift the points on the (D_2) straight line to the (D_1) line. Therefore, we shall subsequently place greater reliance on the coefficients corresponding to (D_1) and we will employ only these in all our discussions. Before proceeding to further exposition, we must make a small detour. The physical chemist, observing empirically a simple relation between

the measured quantity and some theoretical parameters, can adopt two attitudes: he can either take the risky course of remaining blissfully satisfied or he can attempt to show that the relation obtained is in no way due to chance. The first attitude was in fact ours until we decided to adopt the second. More precisely, we adopted this point of view when we were able to show that the magnetic rotation of buta-1,3-diene is a linear function of a sum of the type $\Sigma c_i c_j$ (c_i and c_j are the coefficients of non-adjacent atomic orbitals in molecular orbitals), a sum which represents none other than the ineffective bond indices in the molecule, i.e. the free valence indices. This is valid with sufficient rigour only for aliphatic systems, which we shall call "unsubstituted", where the atoms of the conjugated moiety are linked only to hydrogen or alkyl groups. In fact, it was established that a substituent X other than those mentioned above alters E and ΣI_r to such an extent that the (D_1) straight line cannot be used[62]. However, despite this, one may attempt, by continuing to develop our concepts, to obtain from the data for the Faraday effect extremely interesting results. For example, if we examine a family of compounds of the type R–C=C=C(X) [sic! (Editor of Translation)] (where X = H, CH_3, Cl, OR, or NH_2), it is evident that E varies appreciably as a function of X (Table 10). This is also valid for the series of α-unsaturated carbonyl compounds (Table 11).

Table 10.

Compound	E, μrad	p_{23}
R–C≡C–C(H)=O	18	0.247
R–C≡C–C(R′)=O	12	0.240
R–C≡C–C(OH)=O	25	0.262
R–C≡C–C(Cl)=O	17.5	0.247
R–C≡C–C(NH_2)=O	5	0.232

Castan's classical calculation[63-66] of the π-electronic structure by Julg's method shows that the observed changes in E can be related in both cases to changes in the indices of the "single" (C_2–C_3) bond by expressions of the type

$$E_e = 940\, p_{23} - 253,$$
$$E_a = 810\, p_{23} - 183.$$

The first is valid for ethylene derivatives and the second for acetylene derivatives[67]. The relations are of definite interest from the standpoint of both the Faraday effect and quantum chemistry.

1. They throw light on the apparently random distribution of E values obtained from experimental observations and indicate the extreme sensitivity of the Faraday effect to minute changes in the electronic characteristics of conjugated molecules: thus in ethylene derivatives Δp_{23} of the order of 0.04 of an electron corresponds to a change ΔE of the order of 35 μrad.

2. They make it possible to predict the numerical value of the magnetic rotation for those compounds of the type investigated for which experimental data are not available.

3. They permit a refinement of the Couloumbic integrals and the effect of the substituent X when these are not known with adequate precision. In particular, Castan confirmed the integrals proposed by Peradjordi[68] for the amide group, whereas in the literature there exist discrepancies on this question.

4. Finally, they demonstrate the existence of a definite threshold, in terms of bond indices, beyond which conjugation effects must not be expected in the Faraday effect, namely for ethylene derivatives starting with 0.269 and for acetylene derivatives starting with 0.226.

This unusual result suggests that in an unsaturated system there may be electron delocalisation which is not reflected in the Faraday effect, i.e. the deformation of molecular orbitals under the influence of the magnetic field is too insignificant for observation. The existence of a threshold accounts for the zero exaltation of conjugation in α-diketones; although these compounds are in fact evidently conjugated, their $p_{23} = 0.152$ is significantly below the detection threshold, as shown by Castan and Labarre[69].

Table 11.

Compound	E, μrad	p_{23}
CH_2=CH–C(H)=O	45	0.296
CH_2=CH–C(CH_3)=O	19	0.288
CH_3–CH=CH–C(H)=O	43	0.315
CH_3–CH=CH–C(CH_3)=O R–CH=CH–C(CH_3)=O CH_3–CH=CH–C(R′)=O	35	0.307
CH_3–CH=C(CH_3)–C(H)=O	37	0.308
$(CH_3)_2$C=CH–C(H)=O	54	0.328
CH_2=C(CH_3)–C(H)=O	—	0.288

Having investigated in this way the "linear" conjugated systems, we now consider the behaviour of conjugation exaltation in cyclic systems. The idea underlying the first study in this field by Graffeuil and coworkers[70] is quite analogous to that just discussed. The study was based on a large number of hydrocarbons containing one or several benzene rings. A linear relation was observed between the conjugation exaltation E_{Ar} and ΣI_r with the same initial abscissa as for the (D_1) straight line. However, now the experimental points lie on another straight line (D_2):

$$D_1 \quad E_{Al} = 111\,(\Sigma I_r - 1.464),$$
$$D_2 \quad E_{Ar} = 200\,(\Sigma I_r - 1.464).$$

This implies that, for a conjugated system characterised by the value of ΣI_r, the exaltation E_{Ar} (for cyclic molecules) greatly exceeds E_{Al} (for alicyclic molecules).

$\Delta E = E_{Ar} - E_{Al}$ reflects to some extent the transition from conjugation in open chains to conjugation in rings or to "aromaticity". The existence of ΔE is due to the presence in the aromatic molecule of delocalised π electrons the increased mobility of which under the influence of an applied magnetic field may be observed. Thus we immediately discover that ΔE is due to the Pauling–Pople current characteristic of a cyclic molecule. This hypothesis is the starting point of an exciting study, since under these conditions the Faraday effect constitutes a cardinal method for investigating the entire problem of aromaticity. Moreover, ring currents, as an expression of the magnetic properties of the substance, are as important as the susceptibility and nuclear magnetic resonance, where, incidentally, the existence of the Pauling–Pople current was first demonstrated.

The same conjugation exaltation might also be expected for all aromatic molecules with a specified value of ΣI_r. However, if one examines for this purpose the entire multiplicity of mono- and poly-substituted benzenes, it is immediately seen that such expectation is in vain: Table 12 lists certain values of E obtained in a number of investigations [71-76] and readily shows small deviations upwards and appreciable deviations downwards from 182 μrad, which is characteristic of benzene. It is also evident that for all such molecules ΣI_r remains virtually constant, at least when the calculation is performed in the same way with respect to the benzene ring. The question arises as to the factor, electronic or geometrical, which has such a marked influence on the conjugation exaltation of the molecule and its aromaticity. An answer was obtained after the investigation of the $(\sigma + \pi)$ electronic structures of 60 substituted benzenes, which we calculated ourselves [77-80].

Table 12.

№*	E, μrad	G	№*	E, μrad	G
6	208	0.006	23	147	0.030
1	191	0.031	16	147	0.059
20	187	0.016	24	137	0.063
8	183	0.066	17	130	0.109
21	177	0.037	19	125	0.081
14	176	0.029	7	123	0.088
3	175	0.032	2	91	0.112
4	170	0.083	11	66	0.144
10	166	0.064	5	63	0.138
12	152	0.101	15	59	0.101
9	150	0.071	13	25	0.169
18	148	0.063	22	12	0.159

*The numbering corresponds to the curves in Fig. 4.

The methods of calculation employed were similar [48,77]. One may conclude that, whereas the bond indices are always close to the value (0.667) observed for benzene, the gradient of the $(\sigma + \pi)$ electronic charge localised at the six carbon atoms in the benzene ring deviates more or less appreciably from the zero value which obtains in benzene (Table 12). The charge gradient gives rise to potential barriers at the vertices of the ring, reducing the ability of delocalised π electrons to generate the ring current. It was found that, although the aromaticity of the molecule does evidently depend on the π-electron density, it is also a function of the distribution of σ-electron density. Thus we arrive at Musher's objection to the concept of the ring current, at least in its classical form. The results of our magneto-optical studies show that the molecule can have a high delocalised electron density and nevertheless have no ring current, provided that the gradient G is sufficiently large.

Fig. 4 confirms the validity of the foregoing, since it reveals a very important linear relation between E and G. [81] It should be noted that the definition of G is quite independent of the nature of the atoms in the molecule. Clearly, this quantity can be calculated with equal success for both hydrocarbons and heterocycles, for example pyridine, and for heteroatomic cyclic compounds, for example borazine. Subsequently we shall find it very important to be able to measure the relative aromaticity of the molecule under specified conditions in terms of the quantity G, i.e. to be able to use the same concept to describe both benzene homologues and heterocycles of the same symmetry; this makes it unnecessary to introduce the concept of pseudoaromaticity, so frequently encountered in the literature, when a heteroatom replaces a carbon atom in the ring.

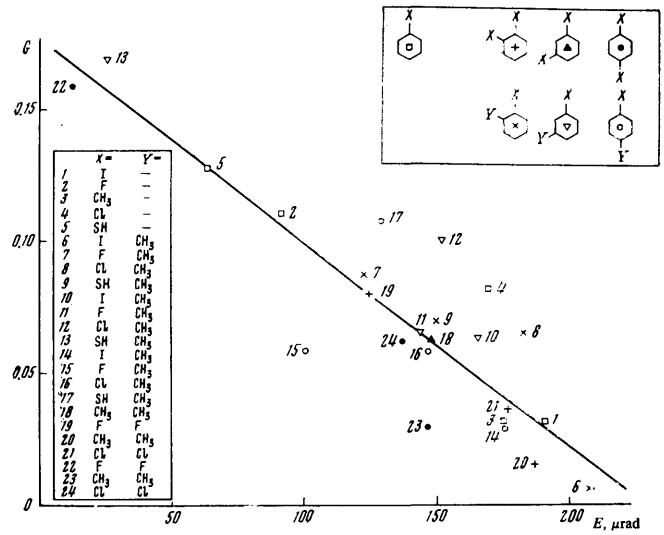


Figure 4.

The sum total of the results led us to the following definition [82]: a cyclic molecule is aromatic when the distribution of the delocalised π electrons is such that they can be put in motion under the influence of an applied magnetic field [in consequence of the absence of an appreciable gradient of the $(\sigma + \pi)$ charge localised at the vertices of the molecule]. The Pauling–Pople current then arises. This aromaticity can be either measured experimentally with the aid of the Faraday effect (the measured E) or predicted theoretically by calculating the $(\sigma + \pi)$ electronic structures (the definition of G and p_{rs}). Thus we have two equivalent means for determining to what extent the molecules belong to a particular type, provided of course that the charge distribution along the ring belongs to the same symmetry group. This conclusion follows from the following observation: when E is expressed as a function of G for compounds belonging (in the sense just described) to the D_{3h} group (borazines and boroxins) [83-85] or to the C_{2v} group (furan, thiophen, etc.) [86], we obtain in each case a linear relation—the corresponding graph is parallel to that shown in Fig. 4. However, for each group the symmetry of the distribution of the localised $(\sigma + \pi)$ charge (at the vertices of the ring), there exists a specific $E = f(G)$ straight line which cannot be made to coincide with the line in Fig. 4 whatever assumptions are made in the calculation. Thus we arrive at Musher's second objection to the ring current. It largely recapitulates the previous postulate.

1. It is impossible to compare the aromaticities of benzene and a molecule which does not belong to the D_{6h} group. Even if we are entitled to measure the aromaticities of substituted benzenes relative to that of benzene itself, this can only be done provided the Coloumbic integrals, correctly estimated from ultraviolet spectra, show

only small deviations from the value of α, as for X = P, Cl, I, and SH; on the other hand, for aminobenzenes we obtain from the ultraviolet spectra $\alpha C(NH_2) = \alpha - 0.6\beta$,[87] which corresponds to a C_{2v} symmetry of the benzene ring rather than D_{6h}.

2. It appears that certain benzene derivatives cannot be classified as aromatic compounds at all. In particular, this applies to fluorobenzene, which has an extremely low value of E_{Ar}, lower than that which benzene should have if it were "aliphatic", i.e. if the ring current were altogether absent. Clearly, we hesitated for a long time before publishing such a surprising conclusion. Our doubts continued until we recognised that fluorobenzenes are nitrated and sulphonated with difficulty‡, which may be regarded as a chemical criterion of the quasi-non-aromaticity of fluorobenzene.

We have discussed thoroughly the problem of the aromaticity of substituted benzenes. However, the rule which we have proposed is evidently general: we have used it also to solve the problem of the aromaticity of substituted borazines and boroxins of D_{3h} symmetry—the problem which has been the subject of controversy, as shown by the literature. We calculated the $(\sigma + \pi)$ electronic structure of molecules of this type, the magnetic properties of which have been investigated systematically by Laurent and coworkers[88-91] and the relative aromaticity scale, which we obtained using the calculated values of G, is very satisfactorily confirmed by experimental data[92].

The concept of aromaticity in terms of our definition was then applied[86] to pentagonal heterocycles of the C_{2v} group. The data obtained yielded the familiar result that pyrrole and furan are virtually non-aromatic, while thiophen is aromatic owing to overlapping of the 3d orbitals of sulphur, which promotes the appearance of a ring current.

We showed that the aromaticity of pyridine is 5–6 times lower than that of its N-oxide[93]. This becomes clear after examining the structure of the (N→O) donor–acceptor bond, which reduces the electron density at the nitrogen atom, while its enhanced value in pyridine is responsible for the potential barrier which prevents the occurrence of a ring current.

Finally, Bonnafous[94] investigated the aromaticity of nitrobenzenes and nitrotoluenes[94]. However, this problem, which is associated with the nature and magneto-optical properties of coordination bonds, will be set aside for discussion in the appropriate section.

Another magneto-optical criterion of aromaticity, for which we had great hopes in 1967 bearing in mind its operational simplicity, was discussed similarly. This criterion was suggested by Zimmerman and Foster's NMR experiments[95]: they showed that the signal due to benzene protons is displaced towards weaker fields on diluting benzene with a chemically inert solvent and Pople suggested that this may be due to a change in the ring current on dilution[96]. A similar experiment by Crasnier on the Faraday effect showed that the molecular magnetic rotation of benzene decreases exactly linearly on dilution by a solvent such as hexane. We believed that we had a simple means for measuring the "intensity" of the ring current in the molecule and became even more firmly convinced of this after a study[82] showing that the corresponding decrease in the above solvents is greater the greater is the initial "intensity". The first measurements for fluorobenzene, p-difluorobenzene, chlorobenzene, and bromobenzene, in n-hexane solution[82] enabled us to establish a relative aromaticity scale identical with that which is deduced from the measurements of E and calculations of G. However, this agreement gradually disappeared as the number of molecules investigated increased and soon it was necessary to conclude that the straight line obtained for a given aromatic compound (see iodobenzene[80]) varies from one solvent to another so much that we are simply unable to take into account the solute–solvent chemical interaction. Precisely because of these considerations, we undertook a new study of the criterion of aromaticity "in solution" by measuring the molecular rotation of benzene in 16 solvents; the results[97] are presented in Fig. 5 and in Table 13.

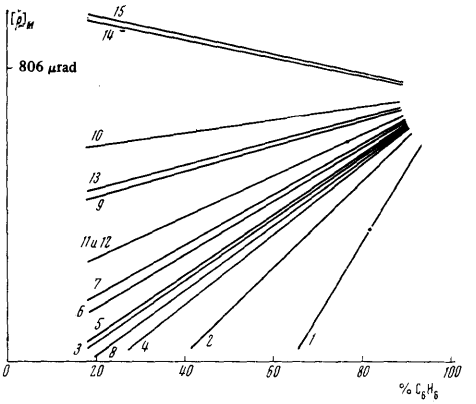


Figure 5.

Table 13.

No.	Solvent	Equation	r	n_D^{20}	P
1	Trifluoroethanol	$y=0.856\ x+730.3$	0.99	1.2910	0.182
2	Methanol	$y=0.498\ x+762.8$	0.99	1.3288	0.203
3	Ethyl ether	$y=0.346\ x+773.8$	0.99	1.3526	0.217
4	Ethanol	$y=0.399\ x+771.5$	0.99	1.3611	0.221
5	n-Hexane	$y=0.338\ x+773.0$	0.99	1.3749	0.229
6	Isopropyl alcohol	$y=0.294\ x+779.2$	0.98	1.3776	0.230
	1-Propanol	$y=0.287\ x+781.0$	0.99	1.3850	0.234
7	Iso-octane	$y=0.358\ x+773.4$	0.99	1.3915	0.238
8	Tetrahydrofuran	$y=0.140\ x+794.0$	0.96	1.4076	0.247
9	Dioxan	$y=0.072\ x+801.9$	0.95	1.4224	0.254
10	Cyclohexane	$y=0.229\ x+787.2$	0.99	1.4266	0.257
11	Dimethyl formamide	$y=0.231\ x+788.9$	0.97	1.4269	0.257
12	Chloroform	$y=0.130\ x+798.3$	0.99	1.4433	0.265
13	Carbon tetrachloride	$y=-0.103\ x+818.5$	0.97	1.4601	0.274
14	Dimethyl sulphoxide	$y=-0.111\ x+819.9$	0.99	1.4780	0.284

*The numbering corresponds to the curves in Fig. 5.

They require the following comments. (1) The variation of $(\rho)_M$ is exactly linear over a wide range of concentrations, which is confirmed by the correlation coefficients r; (2) however, the decrease observed for hexane, on which earlier we intended to base the criterion of aromaticity in solution, is by no means general—in particular, it is evident that in certain cases there is an increase and not a decrease of $(\rho)_M$; (3) as regards the order in which the solvents investigated can be arranged, it is at first sight difficult to grasp whether, for example, their macroscopic

‡ Electrophilic substitution reactions of fluorobenzene (including nitration) are well known, see, for example, Stock and Brown[186] (Editor).

polarisability is an appreciable factor or not—from this point of view it is surprising that carbon tetrachloride and dimethyl sulphoxide give similar experimental relations.

It is customary to say that the solute–solvent interaction depends directly on the polarity and the polarisability of the components of the system under consideration. Bearing this in mind, it was logical to check whether the changes in $(\rho)_M$ are a function of polarisability. For each solvent, we calculated the molecular polarisability P from the Lorentz formula

$$P = \frac{(n_D^{20})^2 - 1}{(n_D^{20})^2 + 2}$$

and showed (Fig. 6) that there is a significantly linear relation between P and the experimental data for the Faraday effect[97]. However, it is evident that the decrease of $(\rho)_M$ does not depend directly, as might have been expected, on the "intensity" of the ring current in the molecule when the substance is diluted but is more likely to be associated with solute–solvent interactions, which cause a more or less pronounced change in the internal electric field. The overall effect of the internal electric field and the external magnetic field is in fact observed. Hence one must assume that the investigation of "aromatic" molecules in solution by the magneto-optical method cannot yield a criterion of aromaticity. However, this conclusion must be extended also to the results of analogous NMR studies, as suggested simultaneously both by our group[67] and by Falk and coworkers[98].

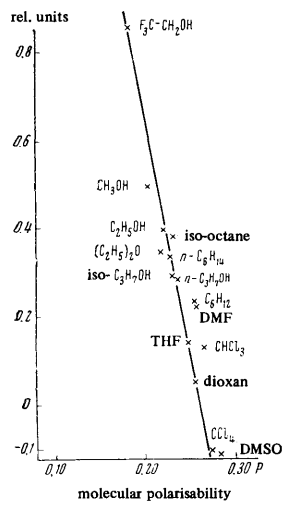


Figure 6.

Some Comments on the Term Aromaticity

We have just seen that measurements of the Faraday effect on the one hand and the knowledge of electronic structures on the other permit the determination of the relative aromaticity of the molecule by a method which is extremely similar to that employed in NMR, i.e. on the basis of the ring current concept.

However, it is quite evident that aromaticity does not always imply the presence of a ring current. Organic chemists will recall the tendency of the molecule to undergo nitration and sulphonation, while to others aromaticity implies the equality of bond lengths, high stabilisation energy, enhanced diamagnetic anisotropy, ultraviolet absorption very close to the visible region, and finally intense spin delocalisation (in ions and radicals). Nevertheless, it appears clear that the word aromaticity has lost any kind of simple significance and that we are unable to give it a true definition. An additional difficulty arises because we cannot measure the aromaticity of the molecule and even relative scales based on the measurements of various chemical and physical properties are not absolutely consistent.

From our standpoint, the time has now come to reject the use of the term aromaticity in order to eradicate from speech and print the ambiguity which consists in the postulate that "aromatic means benzene-like and conversely". In fact we have already seen that certain substituted benzenes characterised by a low value of E and a large gradient G cannot be classified as aromatic. Our suggestion that the term aromatic be rejected should also be welcomed because there exist numerous prefixes (non-, anti-, quasi-, pseudo-, homo-, ...) to this term. Clearly "the time is now right" for this. However, as mentioned by Coulson[99], the problem does not consist in finding a new word to replace the term aromaticity: it appears preferable to introduce a series of new concepts such that each should refer to one of the numerous chemical or physical properties the sum of which makes it possible to comprehend the essential features of aromaticity. On the basis of these considerations, we suggest that the concept of "potential strobilism" be adopted to describe the property measured both in connection with the Faraday effect and in NMR in studies on planar cyclic molecules with delocalised π electrons, i.e. when there is a ring current. Thus the strobilism has a potential existence in the molecule and can be discovered by the investigator by applying an external magnetic field. Since the strobilism is a potential property of the molecule in an unperturbed state, one may postulate a direct relation between it and the electronic and geometrical characteristics of the ground state: the distribution of both σ and π electrons, group symmetry, etc.

In conclusion[81] we should like everyone to be clear about the essential nature of our demarche: physicists and chemists observe different effects of "aromaticity"—a pleasant smell, capacity for nitration and sulphonation, a ring current, magneto-optical exaltation, and diamagnetic resonance energy (incidentally this is more of a mathematical term). However, no one can answer the problem whether or not these are consequences of the same property.

In the first place it is extremely desirable to define and express quantitatively the information which each particular method can yield. The various refined concepts will be combined spontaneously provided this is possible in principle.

VI. THE FARADAY EFFECT AND THREE-DIMENSIONAL CONJUGATION

We have already seen that the Faraday effect makes it possible to observe and analyse very refined phenomena of classical electronic delocalisation. However, it must

be emphasised that other methods also allow this—naturally with varying success. However, there is one field where the magnetic rotation of polarisation occupies a privileged position and we should like to devote a few lines to this. Whilst attending in 1967 a seminar in Paris held by Prof. Heilbronner, we heard for the first time of the phenomenon of "three-dimensional conjugation". The exceptionally unusual ultraviolet spectroscopic behaviour of 5,6-diphenylnaphthacene or rubrene was discussed: it exhibits an anomalously large bathochromic shift compared with naphthacene, although it is known that owing to steric hindrance the phenyl groups in the 5- and 6-positions are virtually perpendicular to the plane of the polyacene. It followed from the discussion that the magnitude of the observed effect can be accounted for only by the axial overlapping of the $2p_z$ orbitals of the benzene rings, which imparts to the molecule a three-dimensional resonant structure. We immediately wished to discover whether or not this phenomenon can be observed by means of the Faraday effect and, apart from rubrene, concentrated attention on simpler molecules where three-dimensional conjugation might be expected on general grounds—for example cyclo-octatetraene. This compound exists in the form of a "tube" with D_{2d} symmetry; the carbon–carbon bonds are alternately 1.50 and 1.35 Å long, which indicates the absence of delocalisation of the ring π electrons. Thus, using the general relations of the Faraday effect, we should obtain an experimental molecular magnetic rotation lower than or at least equal to the theoretical value (821 μrad) obtained from additivity. However, in fact the experimental rotation (1008 μrad) exceeds by 187 μrad the expected value. In the present state of our knowledge, such appreciable exaltation of the magnetic rotation compared with the value observed for benzene (182 μrad) can only be explained by three-dimensional conjugation analogous to that in the case of rubrene. Together with Chalvet[100], we succeeded in showing that this kind of exaltation of the Faraday effect corresponds to an overlap integral $S(2p_\sigma, 2p_\sigma)$ smaller approximately by a factor of 2 than for rubrene. This agrees satisfactorily with the intramolecular distances in the compounds under discussion.

Preliminary results of this kind led us to attempt the use of the Faraday effect for the solution of problems in conformational analysis. There are no literature data on the geometrical structure of cyclo-octa-1,4-diene at 20°C. This molecule can exist either in the chair or in the boat form or can oscillate rapidly between them. However, the experimental molecular magnetic rotation is exactly equal to the theoretical value and apparently suggests that cyclo-octa-1,4-diene is planar at 20°C. This is one of the most exciting fields of study for the Faraday effect. So far we have not investigated classical molecules with a geometry allowing possible three-dimensional conjugation (we may refer to Daudel[101]) in view of the lack of the necessary specimens. We hope that our readers will include chemists who will become interested in the possibility of investigating three-dimensional conjugation using the Faraday effect and will be kind enough to get in touch with us in connection with this problem.

VII. DONOR–ACCEPTOR σ-BONDS

Previously we considered in detail how electron delocalisation in diamagnetic compounds containing only normal covalent bonds influences the Faraday effect. Deviations from additivity are observed also when one is dealing with a molecular structure containing a coordinate bond and we shall now discuss the most important features of this phenomenon. As early as 1957, Laurent was the first to undertake a series of studies[102–105] on the electronic nature of the coordinate bonds in compounds of boron halides (Lewis acids) with bases. Complexes of this type should indeed be investigated first, since they provide a rare example of a coordinate bond of purely σ type. Gallais and Laurent suggested that the formation of a $(D^+ - {}^-A)$ coordinate bond (using Lowry's notation) between a base (LMND) and an acid (XYZA) be characterised in terms of the magneto-optical constant equal to the difference $\Delta\rho$ between the molecular magnetic rotation of the complex and the sum of the molecular quantities referring to the pure initial compounds:

$$\Delta\rho = (\rho)_M(\mathrm{LMND^+ - {}^-AXYZ}) - [(\rho)_M(\mathrm{LMND}) + (\rho)_M(\mathrm{AXYZ})] .$$

Table 14.

Compound	Δρ, μrad	Compound	Δρ, μrad
$F_3B \cdot NR_3$	−506	$R_3Al \cdot PR_3$	− 94
$Cl_3B \cdot NR_3$	−140	$Br_3Al \cdot PR_3$	+ 79
$F_3B \cdot PR_3$	−535	$R_3Al \cdot OR_2$	+ 17
$Cl_3B \cdot PR_3$	−164	$Br_3Al \cdot OR_2$	− 33
$F_3B \cdot OR_2$	−350	$R_3Al \cdot SR_2$	+ 49
$Cl_3B \cdot OR_2$	− 23	$Br_3Al \cdot SR_2$	+ 86
$F_3B \cdot SR_2$	−350	$R_3Ga \cdot NR_3$	−130
$Cl_3B \cdot SR_2$	− 26	$R_3Ga \cdot PR_3$	−200
$Br_3Al \cdot NR_3$	−234	$R_3Ga \cdot OR_2$	− 85
$Br_3Al \cdot NH_3$	+ 35	$R_3Ga \cdot SR_2$	− 52

The important findings arising from such a treatment are the virtually permanently negative sign of $\Delta\rho$ and its large absolute value (Table 14). The analogous studies for aluminium compounds by Gallais and de Loth[31] and for gallium compounds by Laurent et al.[106] made it possible to extend the initial conclusions. Usually the absolute values obtained for $\Delta\rho$ were lower than those measured by Laurent for complexes based on BF_3. The authors concluded that, when a covalent bond leads to a negative value of the magneto-optical constant as defined above, the most likely reason is donor–acceptor interaction. At the same time it is evident that $\Delta\rho$ reflects not only the rotation due to the donor–acceptor bond but also the magneto-optical effect associated with all the changes occurring when the donor atom is attached to the acceptor atom. We endeavoured to separate the various factors contributing to $\Delta\rho$ and attempted to specify in each case the corresponding effects in order to isolate in a pure form from $\Delta\rho$ the magnetic rotation $\rho(D^+ - {}^-A)$ due to the donor–acceptor bond[107]. This is particularly necessary, since the negative sign of $\Delta\rho$ does not correspond to the formation of diamagnetic complexes. It has been shown[108,109] that purely magnetic rotation due to the $(D^+ - {}^-A)$ σ bond should be positive. The considerable decrease of magnetic rotation is due to secondary effects in the formation of such a bond. A complete examination of the secondary factors governing the change $\Delta\rho$ leads not only to an estimation of the purely magnetic rotation due to $(D^+ - {}^-A)$ bonds but also to a fairly complex analysis of the coordination phenomenon as a whole. More precisely, the postulate that $\rho(D^+ - {}^-A) \geqslant 0$ makes it necessary to estimate in each specific case the importance of the secondary factors and poses the problem of the multiplicity of the $(D^+ - {}^-A)$ bonds.

The most permanent of the secondary factors which may be taken into account directly in the Faraday effect is the marked decrease of the magnetic polarisability when a free electron pair of the donor atom is converted into an electron pair involved directly in bond formation. This is particularly important since donor–acceptor bonds are usually characterised by considerable charge transfer[110,111]. This marked decrease of polarisability, which leads to a decrease of the magnetic rotation in certain cases, is sufficient to account for the negative sign of $\Delta\rho$. As an example, we shall consider the compounds $R_3Al.PR_3$ ($\Delta\rho$ = −94 μrad). We know the contribution $\rho(d\mathrm{P})$ by the free electron pair of the donor atom (+255 μrad) assuming sp^3 hybridisation of the phosphorus atom[39]. Assuming that at the instant of formation of the complex, the free electron pair is replaced by the paired bonding electrons, we find that the rotation due to the ($P^+-{}^-Al$) bond is

$$\Delta\rho = 255 + \rho(P^+-{}^-Al) = -94 \ \mu\text{rad},$$
$$\rho(P^+-{}^-Al) = -94 + 255 = +161 \ \mu\text{rad},$$

i.e. is positive.

Table 15.

Compound	$-\rho(d_P)$	$\delta G^{C_{3v}}_{D_{3h}}$	$-\pi_{AXYZ}$	$\rho(D^+-{}^-A)$	$\Delta\rho$
$R_3Ga\cdot OR_2$	0	−85	0	0	− 85
$R_3Ga\cdot NR_3$	− 86	−85	0	+ 41	−130
$R_3Ga\cdot PR_3$	−255	−85	0	+140	−200
$Cl_3B\cdot OP_2$	0	−23	0	0	23
$Cl_3B\cdot SR_2$	− 52	−23	0	+ 49	− 26
$Cl_3B\cdot PR_3$	−255	−23	0	+114	−164

However, the above considerations are not sufficiently general, because many factors which frequently play a major role have not been taken into account. For the case of a purely σ donor–acceptor bond, we shall recall the most important of these: (a) the formation of the complex is frequently accompanied by a change in hybridisation and in the partial ionic character; we shall denote this by δG in order to recall the change in the symmetry group; this applies equally to a Lewis base and acid; (b) the multiplicity of the normal covalent bond (π_{AXYZ} and π_{DLMN}) in isolated donor and acceptor molecules is also altered at the instant of the formation of the complex§. Table 15 shows how important are these two factors. We shall consider initially the compound R_3GaOR_2 for which $\Delta\rho$ = −85 μrad. Then, as incidentally for all complexes containing an ($O^+-{}^-A$) bond, one may postulate that the electron pair of the oxygen atom is involved in the formation of this bond and hardly plays any [other] part; earlier we concluded that even the magnetic rotation due to the lone electron pair of the oxygen atom is close to zero[39]. In this situation [all the (GaR) bonds are undoubtedly single] one must postulate that the decrease of the magnetic rotation in the Faraday effect expressed by $\Delta\rho$ can only be due to factor a [when $\rho(O^+-{}^-Ga) \geqslant 0$ is postulated]. Essentially the sp^2 hybridisation of the gallium atom in GaR_3 monomer becomes close to the sp^3 hybridisation in the complex. This change is accompanied by a decrease in the polarisability of the (Ga–C) σ bonds, which, as we have shown earlier, always reduces the magnetic rotation. Expressing this by

$$(|\delta G|^{C_{3v}}_{D_{3v}}),$$

we find that in this case δG = −85 μrad.

If we consider further other gallium compounds ($R_3Ga.PR_3$, $R_3Ga.NR_3$), the use of the value of δG obtained for the second factor and the magnetic rotations due to the lone electron pairs of the phosphorus (about 255 μrad) and nitrogen (about 86 μrad) atoms yields positive values for the true rotation due to the ($P^+-{}^-Ga$) and ($N^+-{}^-Ga$) bonds¶. Similar considerations apply also to the compound $Cl_3B.OR_2$, for which $(\delta G|^{C_{3v}}_{D_{3h}}) = 2-23$ μrad†. In general this result is consistent with the higher magnetic polarisability of the (Ga–X) bond compared with (B–X). If we now substitute the value −23 μrad in the expression for $\Delta\rho$ for the compounds $Cl_3B.SR_2$ and $Cl_3B.PR_3$, we obtain for the true magnetic rotation due to the ($S^+-{}^-B$) and ($P^+-{}^-B$) bonds positive values of ρ (+49 and +114 μrad), which are lower than the corresponding contribution $\rho(d\mathrm{S})$ and $\rho(d\mathrm{P})$ due to the lone pairs.

The effect of the factor b (the multiplicity of the bonds in isolated molecules of the donor or acceptor) is clearly shown in complexes based on BF_3. It has long been known that $\Delta\rho$ for such complexes is much higher than for the analogous complexes with BCl_3.[102]

Table 16.

Compound	$-\rho(d_D)$	$\delta G^{C_{3v}}_{D_{3h}}$	$-\pi_{AXYZ}$	$\rho(D^+-{}^-A)$	$\Delta\rho$
$F_3B\cdot OR_2$	0	−23	−327	0	−350
$F_3B\cdot SR_2$	− 52	−23	−327	+32	−370
$F_3B\cdot PR_2$	−255	−23	−327	+70	−535

Table 16 shows how $\Delta\rho$ may be used to obtain the constants for the ($D^+-{}^-A$) bonds for certain BF_3 complexes. Assuming that to a first approximation the factor

$$|\delta G|^{C_{3v}}_{D_{3h}},$$

is constant for both BF_3 and BCl_3, the formation of $F_3B.OR_2$ will differ from that of $Cl_3B.OR_2$ only due to the disappearance of the double bond character of the (F–B) bonds on transition from the isolated BF_3 molecule to the complex‡. This process leads to a decrease of the magnetic rotation by 327 μrad, which agrees only in order of magnitude with the real rotation (416 μrad) observed, for

§ The bases NR_3, PR_3, OR_2, and SR_2 have been investigated; evidently π_{DLMN} is zero in all cases. We also suggest that δG is negligibly small for these bases, because there is virtually no change in hybridisation.

¶ For example $\rho(N^+-{}^-Ga) = \Delta\rho + \rho(d_N) - \delta G = -130 + 86 + 85 = +41$ μrad.

† When the multiplicity of the (B–Cl) bond in an isolated BCl_3 molecule is neglected.

‡ The considerable double bond character of the B–X bond has been confirmed by the large changes in the asymmetry parameter (η = 45% for B–Br and η = 45% for B–I in BX_3 with respect to X, which corresponds to amounts of double bond character of 13.3 and 15.6%)[127,188] (Editor).

example, for $R_nBF_{3-n}.NR'_3$.[112] Thus we have to recognise the existence in this case, as incidentally also in certain others discussed below, of a third factor responsible for the high negative value of the observed $\Delta\rho$. We now substitute $\pi_{BF_3} = -327$ μrad in the expression for $\Delta\rho$ for the compounds $F_3B.SR_2$ and $F_3B.PR_3$; this leads to positive values of $\rho(S^+-{}^-B)$ and $\rho(P^+-{}^-B)$ lower than the corresponding $\rho(d_S)$ and $\rho(dp)$. It is interesting to note that the results for the $(P^+-{}^-B)$ bond were obtained[113] from a study of the magneto-optical properties of the compounds $H_3B.PR_3$ by means of an analysis which differs significantly from that described above. In the compounds investigated $\Delta\rho \simeq -480$ μrad and the relative contributions by factors which must be taken into account are $-\rho(d_P) = -255$ μrad, $(\pi_{AXYZ}) = 0$, and $-\delta G = -300$ μrad. The resulting value of the modulus $\rho(P^+-{}^-B)$ is positive (+85 μrad) and is the same as that found from a series of $F_3B.PR_3$ compounds. Nevertheless there is a significant difference between the contributions of the factors constituting $\Delta\rho$ on passing from $F_3B.PR_3$ or $Cl_3B.PR_3$ to $H_3B.PR_3$: in the latter case the δG term is very large, so that the homopolarity of the (B–H) bond entails a high value of the b_{BH} coefficient[50] and a large change in it on passing from the hypothetical BH_3 molecule to the BH_3 group in the real complex. In conclusion of the first part of the discussion, we may note that we appear to be in a position to explain in specific cases the order of magnitude of the factors contributing to $\Delta\rho$ assuming that the contribution by the donor–acceptor bond in the compounds investigated is positive. The problem of the multiplicity of this bond has clearly remained outside the discussion. The observed large negative values of $\Delta\rho$ can be reasonably accounted for by factors characterised by the negative quantities $-\rho(d_D)$, $-\pi_{AXYZ}$, and $-\delta G$, the last sometimes predominating.

Table 17.

Compound	$-\rho(d_D)$	$\delta G^{C_{3v}}_{D_{3h}}$	$-\pi_{AXYZ}$	$\rho(D^+-{}^-A)+\pi$	$\Sigma(D\cdot A)\ \Delta\rho$
$R_3Al\cdot OR_2$	0	−50	0	+ 67	+17
$R_3Al\cdot SR_2$	−52	−50	0	+151	+49
$R_3Ga\cdot SR_2$	−52	−85	0	+ 85	−52

The general analysis would have to be continued further if there existed a theoretical possibility of a multiple donor–acceptor bond. In the series of compounds in which we are interested such a possibility would exist theoretically if the d orbitals of the acceptor atom could effectively overlap the sp^3 hybridised orbitals of the donor atom. For boron–oxygen and gallium–oxygen bonds, this is excluded on energetic grounds, but is possible for aluminium–oxygen, aluminium–sulphur, and gallium–sulphur bonds. We shall consider from this standpoint the $(O^+-{}^-Al)$ bond in $R_3Al.OR_2$ (Table 17). One lone electron pair on the oxygen atom is involved in the formation of the donor–acceptor bond and the other occupies the $(2s, 2p)$ hybrid orbital, which cannot overlap the $3d$ orbitals of the aluminium atom on symmetry grounds. However, the overlap integral $S(2p, 3d)$, although small (of the order of 0.5 eV) is not zero. Bearing in mind the previous postulates $[\rho(d_0) = 0]$, it follows that $[\rho(O^+-{}^-Al) = 0]$, and, assuming that $\delta G\left|{}^{C_{3v}}_{D_{3h}}\right.$ should be about −50 μrad, we find from the interpolation of the values obtained for boron (−23 μrad) and gallium (−85 μrad) compounds that we can write $\Delta\rho = +17 = \delta G + \pi(OAl)$, whence $\pi(OAl) \simeq 67$ μrad. This value of $\pi(OAl)$ appears to be sufficiently high to reflect some multiplicity of the O–Al bond. In any case, if the $(O^+-{}^-Al)$ bond has some multiplicity, this is even more true of the $(S^+-{}^-Al)$ bond, where the overlap integral $S(3p, 3d)$ is numerically much larger than $S(2p, 3d)$. Indeed, for $R_3Al.SR_2$,

$$\rho(S^+-{}^-Al)+\pi(SAl)=151 \quad \mu\text{rad},$$

and, assuming that the rotation due purely to $(S^+-{}^-Al)$ must be less than or at least equal to $\rho(d_S) = +52$ μrad, we arrive at $\pi(SAl)$ of the order of 100 μrad. This may be interpreted as an increase of the multiplicity of the coordinate bond in sulphur compounds which are isologous with oxygen compounds. Among gallium compounds there also exist examples where the $(D^+-{}^-Ga)$ bonds have a definite π character; this is possible for $R_3Ga.SR_2$ [from the standpoint of the overlap integral $S(3p, 4d)$]. According to Table 17, $\rho(S^+-{}^-Ga) + \pi(SGa) = +85$ μrad; assuming that $\rho(d_S) = +52$ μrad, one must postulate that $\pi(SGa)$ is at least 33 μrad.

Table 18.

Compound	$-\rho(d_D)$	$\delta G^{C_{3v}}_{D_{3h}}$	$-\pi_{AXYZ}$	$\pi(D^+-{}^-A)$	$\rho(D^+-{}^-A)$	$\Delta\rho$
$Cl_3B\cdot NR_3$	−86	−23	0	0	−31	−140
$F_3B\cdot NR_3$	−86	−23	−327	0	−70	−506

We have considered how it is possible to obtain the approximate magnitude of various factors contributing to the overall value of $\Delta\rho$, using a detailed analysis of the mechanism of the formation of the complexes. We emphasise yet again that a significant feature is the hypothesis that the actual magnetic rotation due to the δ or $(\delta+\pi)$ donor–acceptor bond must never be negative. There are, however, several examples for which analysis of $\Delta\rho$ within the framework of the assumptions made here precludes the assignment of a positive magnetic rotation to the donor–acceptor bond. Thus Table 18 shows that the data for the $Cl_3B.NR_3$ and $F_3B.NR_3$ molecules can yield negative $\rho(N^+-{}^-B)$ (−31 and −70 μrad). Possibly the calculation of $\rho(N^+-{}^-B)$ for these compounds is not sufficiently accurate because the rotation due to the (N–C) bonds in the complex differs appreciably from the corresponding value for the isolated NR_3 molecule. In reality, from the standpoint of the Faraday effect, the (N–C) bond is very sensitive even to the replacement of one R by hydrogen. For example, on going from tertiary to secondary and primary amines, there is an appreciable change in rotation[114]. Possibly the presence of the $(N^+-{}^-B)$ bond also affects $\rho(N^+-{}^-B)$, but at the present time we are not in a position to take this into account[115].

VIII. DONOR–ACCEPTOR ($\sigma + \pi$) BONDS

It is clear from the foregoing that the Faraday effect constitutes a physicochemical method which is especially sensitive in the study of donor–acceptor σ bonds on the

one hand and in the detection of π electrons (both localised and delocalised) on the other. Therefore the idea of applying this technique in the investigation of dative bonds, where there is a superposition of a donor–acceptor σ bond and one or several coordinate π bonds, in order to obtain evidence for the multiplicity of dative bonds is extremely attractive. When such a study was planned at the beginning of 1960, the literature of the period contained a relatively large number of papers where it was postulated that certain bonds are of the donor–acceptor $(\sigma + \pi)$ type. We undertook an investigation with the aid of the Faraday effect in order to contribute to the solution of the problem.

A. THE (PO) BOND IN COMPOUNDS OP(XYZ)

The nature of the PO bond like that of oxygen–nonmetal bonds, has been the subject of discussion in the literature from the standpoint of the currently most popular hypotheses and its treatment reflects the general ideas which are dominant at the given time. Initially this bond was thought to be double[116] but later it became described as of the donor–acceptor type when the octet concept prevailed[117]. With progress in the study of geometrical structures, it was, however, found that the (PO) bond is too short to be regarded as single and it became represented as having a definite multiple character[118], which led many investigators to the conclusion that it has double bond character. However, numerous observations are in poor agreement with this somewhat schematic concept. In particular the fact that molecular magnetic rotations of $OP(OH)_3$ and $OPCl_3$ are lower than the corresponding values for $P(OH)_3$ and PCl_3 was observed long ago by Voigt[119]. However, all our knowledge about π bonds shows that π electrons exhibit very high magneto-optical activity and therefore it is quite incomprehensible why $OP(OH)_3$ should have a smaller rotation than $P(OH)_3$ if its structure were indeed represented by the formula $O = P(OH)_3$. The same remark is valid also for any comparisons between OP(XYZ) and P(XYZ).[120] This conclusion inevitably leads to the structure O←P(XYZ) on the basis of numerous examples of complexes in which the formation of a donor–acceptor σ bond leads to an appreciable decrease of the magnetic rotation (cf. the previous section). We can now understand the causes underlying the problem formulated in this way, which we thought interesting to solve with the aid of the Faraday effect. Starting in 1961, Labarre and Voigt undertook the synthesis and magneto-optical study of a large number of compounds of the type P(XYZ) and OP(XYZ).[121–123] Initially the results were interpreted on the basis of additivity, which should obtain in tervalent phosphorus compounds (molecules with covalent diamagnetic σ bonds)[36,37]. Indeed they discovered the relation $\rho = a + bI$, which was already discussed in Section III.[51] They succeeded, together with Gallais, in employing the method involving the resolution of the magnetic rotation of the compound OP(XYZ) into bond constants in order to determine the true magnetic rotation due to the (PO) bond[36,37]. It should be noted that all the geometrical and electronic factors which must be invoked to describe the addition of the oxygen atom to the P(XYZ) molecule were rigorously defined and numerically calculated with a high degree of accuracy[124,125].

Table 19 lists the values of ρ(PO) obtained and it is immediately seen that this quantity depends markedly on the nature of the atoms or groups of atoms attached to phosphorus. It was logical to relate certain changes to the parameters which describe the real electronic structure of the $(\sigma + \pi)$ bond using the classical procedure in quantum chemistry or more precisely to the multiplicity of this bond in our case. Initially we employed the results of Wagner's calculation[126], since the formal mathematical treatment was based on a model of the (PO) bond in which the σ and π bonds were treated as of the donor–acceptor type. Wagner calculated the relevant indices of the (PO) bonds, which ranged from zero for (OPR_3) to two for (OPF_3) (see Table 19).

Table 19.

Compound	p_π (Wagner's data)	p_π (authors' data)	ρ(PO), μrad
OPF_3	1.983	1.911	91
$OP(OR)F_2$	1.682	1.661	88
$OP(OR)_2F$	1.381	1.414	86
$OP(PR)_3$	1.079	1.165	82
$OP(OR)_2Cl$	1.115	0.983	77
$OP(OR)_2R$	0.720	0.778	66
$OP(OR)Cl_2$	1.151	0.621	55
$OPR_2(OR)$	0.360	0.391	40
$ORCl_3$	1.188	0.349	39
OPR_3	0	0.003	0
$OP(SR)_3$	—	0.004	0

In 1967 the existence of a simple and unambiguous relation between the true magnetic rotation ρ(PO) and Wagner's π-bond indices was demonstrated for the entire set of molecules investigated[36,37]. Although the corresponding curve had a maximum, M. C. Labarre, Voigt, and Gallais expressed doubts concerning certain experimental points.

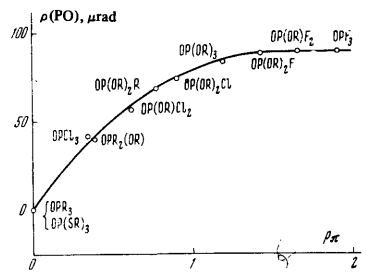


Figure 7.

Therefore Castan and Dagnac-Amans investigated in 1969[124] the electronic structure of OP(XYZ) using a formal treatment very close to Wagner's[126], but, in order to avoid a number of approximations and inaccuracies, they improved significantly the method of calculation. As in the method of Gallais and coworkers[48], the charge transferred via σ bonds was calculated using modified Pauling exponential functions[127]. The new values of the π indices are listed in Table 19 and Fig. 7 shows that the maximum about the existence of which doubts had been expressed has indeed disappeared. It is clear from the foregoing that the monotonic relation between ρ(PO) and p_π in Fig. 7 indicates that the (PO) bond is of the donor–acceptor $(\sigma + \pi)$ type.

B. THE (PS) BOND IN COMPOUNDS SP(XYZ)

The hopeful result from the study of the nature of the PO bond led us to further investigation of other bonds of the $(\sigma + \pi)$ type. For example, M. C. Labarre and Voigt[128,129] made an attempt to determine the nature of the (PS) bond in the compounds SP(XYZ). The data on molecular magnetic rotation made it possible to determine the true rotation due to the (PS) bond in each case and to demonstrate a considerable variation of ρ(PS) as a function of the substituents X, Y, and Z.[36,37] Measurements of the susceptibility[130], refraction[131], and dipole moments[132] confirmed the amplitude and direction of the deviations observed in the Faraday effect but the possible relation $\rho(PS) = f(p_\pi)$, analogous to that found above for ρ(PO) still cannot be obtained in an explicit form because the method of calculation of Castan and Dagnac-Amans is unsuitable for sulphur derivatives [difficulties associated with the calculations of the overlap integrals $S(3p_S, 3dP)$]. On the other hand the multiplicity of the (SO) bond in the compounds OS(XY) and $O_2S(XY)$ can be calculated by the method of Castan and Dagnac-Amans[20,133]. The variation of the calculated bond indices is in this case quite parallel to the variation of the true magnetic rotation due to the (SO) bond, as can be seen from Table 20 and Fig. 8. It should be noted that the method of calculation itself may be better than that proposed by Moffitt in 1950.[134] The calculations showed that there is no abrupt change in the electronic nature of the (SO) bond in the compounds OS(XY) and the same bond in the $O_2S(XY)$ molecule. From the common sense point of view, one may predict that for one sulphur–oxygen bond the variation of multiplicity is a monotonic function of X and Y.[115]

Table 20.

Compound	p_π	p(SO), μrad
OSF_2	1.602	109
SO_3	0.939	134
O_2SF_2	0.908	117
SO_2	0.871	161
$OS(OR)_2$	0.667	102
$O_2S(OH)E$	0.573	99
OSCl(OR)	0.338	73
$O_2S(OR)_2$	0.268	76
$O_2S(OH)_2$	0.237	82
$O_2S(OH)Cl$	0.119	35
$OSCl_2$	0.010	39
O_2SCl_2	0.001	0

Physical chemists and especially infrared spectroscopists have for many years given most contradictory interpretations for one of the donor–acceptor $(\sigma + \pi)$ bonds, namely the (NiP) bond in the tetrahedral complexes $Ni[P(XYZ)]_4$.[135] Even if it were possible to show by various methods that the characteristics of this bond vary appreciably as a function of P(XYZ), it would still be doubtful if such changes are determined by the variation of the contribution by π electrons while, that by σ electrons remains constant, or vice-versa, or finally whether the observed effect is an overall one. In a magneto-optical study of a large number of $Ni[P(XYZ)]_4$ complexes carried out in 1967 by Cassoux and coworkers, it was assumed *a priori* that the investigation may be performed by a method analogous to that employed for the analysis of the (PO) and (SO) bonds using the results of most thoroughly tested quantum-chemical procedures. However, even Ballhausen and Gray, the most outstanding specialists in this problem[136], were unable, as far as we are aware, to obtain a result which satisfied them. Cassoux and coworkers synthesised a large number of nickel complexes and measured the Faraday effect for them[137–140], and, using the principles of additivity and numerical analysis of various geometrical and electronic factors associated with the coordination of four P(XYZ) molecules to the nickel atom, found the true rotation due to the (NiP) bond in each complex. Depending on the nature of the atoms or groups of atoms X, Y, and Z, ρ(NiP) varies. However, it was found that there are in addition deviations of the dispersion of the magnetic rotation from the normal value (the definition was given at the beginning of the review), although the first absorption band in the ultraviolet spectrum is sufficiently distant from the wavelengths observed in the Faraday effect for the complexes to be regarded as necessarily having the normal dispersion (Table 21). This anomaly is well known to specialists in the Faraday effect in the *absorption* region and is characteristic of complexes of transition elements with a high symmetry (T_d and O_h).

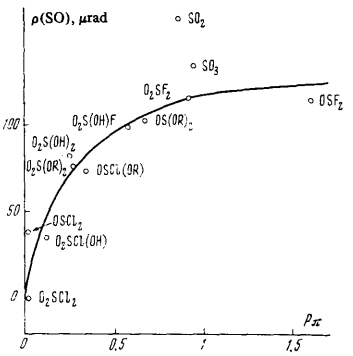


Figure 8.

Table 21.

Compound	ρ (Ni-P)	$\frac{\rho_{545}}{\rho_{578}}$	λ_{max}
$Ni(PCl_3)_4$	1266	1.20	315
$Ni[P(OR)Cl_2]_4$	1157	1.17	284
$Ni[P(OR)_2Cl]_4$	1019	1.16	265
$Ni[P(OR)_3]_4$	871	1.15	237
$Ni[P(OR)_2F]_4$	734	1.15	225
$Ni[P(OR)F_2]_4$	647	1.15	225
$Ni(PF_3)_4$	529	1.15	224

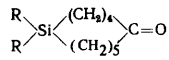
In this case the analysis must be performed not only in terms of the law of additivity but also in terms of the dispersion of the magnetic rotation.[16] Cassoux and coworkers in fact solved the problem in this way. Using Serber's formal treatment[141], they determined the dispersion curve in the region of transparency for A and B (both positive), characteristic of each of the complexes investigated. Then, using the values of A and B, they found the contributions to the magnetic rotation by the σ and π components of the

(NiP) bond[142-144]. It is significant that both contributions vary simultaneously and the multiplicity of the (NiP) bond is in all cases low and variable. These conclusions agree essentially with the results obtained by Bigorgne from infrared spectra[135].

There is yet another special case of a donor–acceptor bond to which a few lines should be devoted, namely the (NO) bond. The electronic structure of the NO_2 group was based for a long time on hypotheses involving mesomerism, i.e. the (NO) bond was regarded as simultaneously a donor–acceptor and a multiple linkage. In fact calculation in terms of such a model does not yield satisfactory results. Its authors asserted, on the basis of certain erroneous assumptions, that with its aid it is possible to obtain the correct dipole moments of such molecules as nitromethane. The reason for this was fortuitous agreement between calculation and experiment without taking into account the contribution by the lone electron pairs of the oxygen atom, which Coulson estimated to be 2D.[145] Therefore in 1967 Bonnafous continued the investigation of the electronic structure of the NO_2 group using this time not mesomeric hypotheses but the more logical Julg model[146]: the group is described in terms of a superposition of two normal (N–O) covalent bonds and a delocalised π system with four electrons: two from the sp^2-hybridised nitrogen atom and one $2p_z$ electron from each sp^2-hybridised oxygen atom. Under these conditions, LCAO calculation of the electronic structure using a calibration based on the ultraviolet spectrum[77] and an iterative procedure[48] yielded a new value of the dipole moment of the NO_2 group, in good agreement with the experimental moment, and also the corresponding absorption bands associated with the $\pi-\pi^*$ transition in the ultraviolet spectrum[147]. It follows from the results of the calculation that the (NO) bond between two atoms with markedly different charges is indeed multiple but the degree of charge transfer in the (NO) bond is 0.25 instead of 0.5 corresponding to the mesomeric concept. The Julg–Bonnafous model agrees most closely with data derived by physicochemical methods (dipole moments, ultraviolet spectroscopy, aromaticity, reactivity) for a large number of compounds, among which we may note nitroethylene[148], nitrobenzene and nitrotoluenes[94], nitropyridines[149], and others.

IX. THE FARADAY EFFECT AND CONFORMATIONAL ANALYSIS

There are certain exceptions from the law of additivity which now give rise to the possibility of investigating conformations with the aid of the Faraday effect. In this field the following important observations have been made: experimental magnetic rotation of cyclopentane, cyclooctane, cyclohexane, and their homologues (Table 22), showing deviations from additivity. In one case this maybe due to steric causes and in another to deviations from a planar structure, which are characteristic of cyclohexane derivatives with fixed carbon atoms in the ring (boat or chair). On general grounds, the decrease of magnetic polarisability in the Faraday effect must be attributed to the characteristics of the configuration, an increase in the barrier to rotation, etc. The law of systematic additivity is known to be fully valid in the absence of steric hindrance for cyclic germanium and silicon compounds with a confused conformation ("pelote).[150] In other cases the strain in the system inevitably leads to experimental magnetic rotations much lower than the theoretical values based on additivity. For example, for the compound



the interaction between the π-electron system of the (C=O) bond and the vacant 3*d* orbitals of the silicon atoms causes a 70% deviation from the theoretical additive value[150]. It is interesting to note that no deviations are observed when the silicon atom is replaced by germanium (this is consistent with self-evident considerations) or by carbon, which indicates that the intensity of the (2*p*, 4*d*) interactions is low. This result agrees fully with the literature: indeed, if the energy levels of the atomic 2*p* orbitals of the carbon atom are much lower than the corresponding levels of the 4*d* orbitals of the silicon atom, the required overlap integral is negligibly small [in particular, the interatomic distances are also large in this case; calculation shows that $S(2p_C, 4d_{Ge}) \simeq 0$]. The foregoing is fully consistent with the semiconductor properties of macromolecules of the type[151]§.

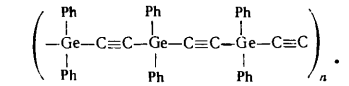
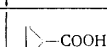
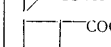
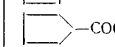
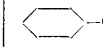


Table 22.

Compound	$[\rho]_M^{exp}$, μrad	$[\rho]_M^{theor}$, μrad	Compound	$[\rho]_M^{exp}$, μrad	$[\rho]_M^{theor}$, μrad
Cyclopentane	349	365		296	303
Cyclopentene	406	427		361	376
Cyclohexane	405	428		421	449
Cyclohexene	451	490		498	522
Cyclo-octane	570	584			
Cyclo-octene	632	646			

One can also postulate that the Faraday effect permits a clear distinction between, for example, the axial and equatorial positions of substituents in cyclohexane, as follows from the depolarisation of diffuse Rayleigh scattering. M. C. Labarre showed that the magnetic rotation of the $C_6H_{11}X$ molecule is a maximum for the equatorial configuration. For the simplest derivatives of cyclohexane, the size of the change in magnetic rotation can reach 15% (X = CH_3, Cl, OH, or NH_2). One can show that the substitution of X = PCl_2 or $P(OR)_2$ takes place preferentially in the axial position in view of the appreciable interaction of the ($P^+-{}^-Cl$) pair with the axial ($C^+-{}^-H$) pair (carbon in the 3-position)[152]. This was quite recently confirmed by electron diffraction for the compound $C_6H_{11}PCl_2$.

§ It is noteworthy that analogous compounds with silicon atoms in the chain also exhibit semiconductor properties. However, the activation energy for conduction in germanium polymers is smaller by a factor of 2 (0.6 and 1.2 eV). The conduction mechanism has still not been explained satisfactorily[189] (Editor).

At the end of the section we must emphasise that there exist two problems in conformational analysis where the Faraday effect can apparently not assist in any way: the classical *cis–trans* isomerism and hydrogen bonding. As regards the first problem, quite hopeful results were obtained by Foehr and Fenske (1949), who made measurements for 2-*cis*- and 2-*trans*-isomers of butadiene (the difference between the magnetic rotations is 7%, [153] which, according to Mulliken's treatment [154], must be attributed to the presence of *cis*- and *trans*-isomers). However, the studies by Castan [155] on a number of acids and esters of α-unsaturated acids showed that the difference between the magnetic rotations of the *cis*- and *trans*-isomers does not exceed 2%, which is quite insufficient to obtain definite results. The same may be said about the studies of hydrogen bonding by the Faraday effect method from the results of the measurements by Gallais and Wolf [156,157] on solutions of various peroxides in chloroform. They observed that the molecular magnetic rotation is insensitive to the presence of the (O...H) hydrogen bond in the series of compounds investigation. On the other hand, analysis of the aromaticity of various phenols and their ethers with the aid of the Faraday effect demonstrated its insensitivity to intramolecular hydrogen bonding.

X. THE FARADAY EFFECT AND THE STUDY OF NON-ISOLATED COMPLEXES IN SOLUTIONS

Earlier we showed that, with certain exceptions, the magnetic rotation in the Faraday effect corresponds exactly to additivity. However, this applies equally to mixtures of substances, at least when there are no solute–solvent interactions. Then, according to the Verdet law,

$$\rho = \sum_0^k \rho_k v_k \left(c \sum_0^k v_k = 1 \text{ ml} \right),$$

where ρ is the Verdet constant for the mixture of substances and ρ_k is the constant for each component. The above relation has been the subject of numerous refinements and tests; we may quote as historical references the work of Schonrock [158], de Mallemann and coworkers [159,160], Hori and Okazaki [161], and Andersen and Asmussen [162]. We may suppose that, when deviations from additivity are observed, we are dealing with chemical interactions between the various substances in the mixture. Numerous deviations from additivity observed in the work of Gallais and coworkers between 1936 and 1952 make it possible to identify and detect non-isolatable complexes, which is sometimes impossible by other methods, particularly polarography. We may point to tetraiodomercurates [163], iodobismuthates [164], thiocyanatomercurates [165–167], bismuth thiosulphates [168], bismuth(III) thiocyanates [169], etc. as examples. In this case the Faraday effect permits a reliable detection of the complex in the mixture [170,171]. The method can be also successfully employed to refine the mechanisms of the neutralisation of acids by bases [172]. Recently R_nGaCl_{3-n} complexes with aliphatic amines were successfully investigated [173].

XI. THE FARADAY EFFECT AND VAN VLECK FERROMAGNETISM

Finally we shall consider a completely specific case of deviations from additivity. It has now been known for 100 years that, despite its diamagnetism, the covalent compound $TiCl_4$ exhibits a negative Faraday effect both in the liquid [174–176] and in the vapour [177]. This is also true of $TiBr_4$. [178] However, as far as we are aware, up to 1968 no other example of molecules with an electron deficit showing an analogous behaviour in its magnetic rotation has been discovered, except for the permanganate ion [179], for which, according to the Faraday effect, a temperature independent van Fleck paramagnetism could be postulated [180]. Stone [181] showed that the positions of the ground and excited electronic energy levels explain the negative paramagnetic contribution to the magnetic rotation. For $TiCl_4$, this paramagnetic contribution may be dominant when certain postulates are made. The studies by Gervais et al. [108] on a series of covalent titanium(IV) compounds led to the conclusion that the (TiO) bond is also characterised by a negative constant for magnetic rotation and resembles in this sense the (TiCl) and (TiBr) bonds. In a study on the magneto-optical and magnetic properties of $TiCl_3OR$, Choukroun and Gervais [182] found that the $OTiCl_3$ group is responsible for paramagnetism of the van Vleck type due to the (TiCl) and (TiO) bonds. Gervais interpreted [183] additional studies on the Faraday effect in the visible region for the compounds $Ti(OR)_4$ from the standpoint of the dispersion associated with the TiO_4 group,

$$\frac{v^2}{(v^2 - v_0^2)^2}$$

in accordance with the term V_A in Serber's formula [141].

In the latest studies by Gervais and coworkers, the complexes of $TiCl_4$ [109] and $ROTiCl_3$ [184] with various alkyl orthotitanates were investigated. The study of the magneto-optical properties in the transparency range of complexes of transition elements with a high degree of symmetry must be accompanied by measurements in the absorption range. A monograph by Schatz and MacCaffery [16] deals with the Faraday effect in the absorption region.

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Thus the Faraday effect in the transparent region constitutes a characteristic physicochemical method capable of solving important problems in structural chemistry. The overall molecular magnetic rotation may be resolved on the basis of the additivity of the properties of matter into a series of components—naturally within the framework of certain postulates. An analogous assignment of various characteristic constants to definite chemical bonds is used also in other spectroscopic methods. On the other hand, all experimental deviations from additivity provide an effective means for investigating a wide variety of problems such as the delocalisation of π electrons in conjugation, the structure of donor–acceptor (σ) and ($\sigma + \pi$) bonds, molecular conformation, and finally temperature-independent paramagnetism when a transition element is involved in certain bonds.

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Raman Scattering and Conjugation

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This review presents the results of recent work on the nature of the Raman scattering of light and on the relation between the parameters of the Raman lines and other molecular constants; the problems encountered in applying line intensity data to studies of the interaction of atomic groupings in organic molecules are discussed in detail. Various types of conjugation are considered, including the effect of substituent atoms on π-bond systems (with special reference to the position of the atoms in the Periodic Table), and the possibility of characterising molecular fragments in the presence and in the absence of conjugation. 328 references.

I. INTRODUCTION

The study of mutual interactions of atomic groups in polyatomic molecules is one of the most important problems in organic chemistry. This approach offers a relatively compact description of a vast multitude of experimental data, and thus enables available data to be applied more effectively to the production of compounds possessing desired properties. It is no exaggeration to say that if the properties of complex molecules could be described by a simple additive scheme the whole of organic chemistry would be reduced to a set of tables of increments, similar to the table of refractive index increments. In practice, however, the number of compounds showing specific properties is almost inexhaustible —this arises from the mutual interactions of atomic groups, which are difficult to study partly because of the complexity of the overall picture and partly because of the limitations of the various methods of investigation. It is desirable, therefore, to carry out combined physical and chemical studies, including atomic vibration spectroscopy (Raman and infrared spectra).

The Raman spectrum consists of a set of lines with frequencies $\nu - \omega_m$, in the vicinity of the exciting line ν. The normal vibration frequencies ω_m of the atoms in the molecule can be used to determine the elastic coefficients of the chemical bonds and the interaction coefficients.

Recent advances in the techniques of Raman spectroscopy—in particular the advent of spectrometers using laser radiation (see Refs. 1-3)—have considerably extended the scope of the method. Spectra can now be obtained from crystalline powders [4-8], polymers [9,10], coloured compounds, and also from samples available in very small quantities (a few mg, and in some cases as little as 0.001 mg). [6,11-13] Line intensities have been measured with solid [5,7] and gaseous samples, and the resolution of closely spaced lines has been improved (see for example Fig. 1). The use of laser light facilitates measurements at low frequencies (see Fig. 2) and allows fast processes to be studied with measurement times of the order of a millisecond [14].

Contrasting the relative advantages of Raman and infrared spectroscopy, we note that the strongest lines in the Raman spectra of symmetrical molecules are those due to totally symmetric vibrations. In keeping with their polarisation, they show little broadening associated with a latent or apparent rotational structure [15,16], and their half-width usually lies in the range 2-20 cm^{-1}. [16-18,24] Conversely, the strongest bands in infrared spectra are those due to antisymmetric vibrations, and also those of strongly polar bonds, which are broadened not only by the rotational motions of the molecules but also by the greater sensitivity of their frequency to intermolecular interactions.

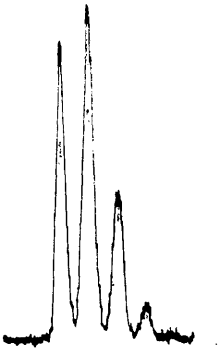


Figure 1. Fine (isotopic) structure of the ~460 cm^{-1} line of CCl_4 at 77°K.

Considering the differentials of the dipole moment $d\mu/dQ_m$ and $d^2\mu/dQ_m^2$ (where Q is the normal nuclear coordinate), we may conclude that the stronger an infrared spectral band is, the more likely it is to be broadened in the case of liquids [19]. Furthermore, overtones are relatively more intense in infrared spectra, and they give rise to more overlapping lines.

Whereas the frequencies observed in infrared and Raman spectra are largely duplicate information, the same is far from being true of the line intensities. It must be admitted, however, that most workers report only qualitative assessments of the intensity ratio of Raman lines for individual spectra: these are useful for assigning the lines, but they cannot be used to compare the lines of different compounds. A universal, objective scale of molar intensities, proposed [17] in 1940, defined the rational conditions for a quantitative comparison of the intensities of lines of different compounds, and made it possible to examine different groups of organic compounds.

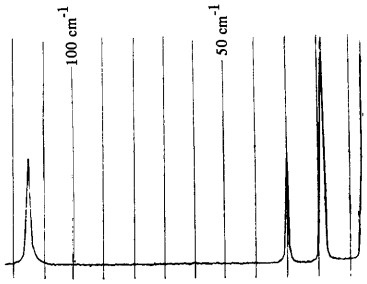


Figure 2. HgI_2 spectrum (He–Ne laser spectrometer). Curves kindly supplied by Dr. E. da Silva (France).

Molar intensity measurements are reproducible, and are an important characteristic of Raman lines. They offer useful additional information on the structure of molecules, on the properties of chemical bonds, on the mutual effects of atomic groups in complex molecules, on electronic excitation levels, on the vibrational modes associated with particular lines [15,16], and on the quantitative composition of mixtures of compounds [17,20,21,24]. Many interesting relationships have been established, and it has been shown that the intensity is one of the parameters most sensitive to conjugation.

This review is particularly concerned with applications of line intensity measurements to studies of the interaction of atomic groups: the relevant literature will be surveyed in the sections devoted to the nature of Raman scattering and to the interrelation between line intensity and other molecular constants.

II. GENERAL VIEWS ON THE NATURE OF RAMAN SCATTERING. SEMICLASSICAL THEORY

The basic Raman parameters can be described by classical theory, by quantum mechanics, or by quantum electrodynamics. Depending on the circumstances, it may be preferable to use one or other of these approaches, or to combine some of their features.

In studies of the line intensities (I_m) of colourless compounds it is usually possible to confine the discussion to the simplest variant of the classical theory, in which one considers the vibrations of the dipole $\mu(t)$ resulting from the polarisation of the electronic shell of the molecule by the field of the light wave. The intensity of the Raman lines depends on the depth of modulation of $\mu(t)$, produced by the vibrations of the nuclei, defined as $\frac{\partial\alpha}{\partial q}$. q_0 for diatomic molecules, and $\frac{\partial\alpha}{\partial Q_m}$. Q_{0m}, for polyatomic molecules, where α is the polarisability of the molecule, q is the change in interatomic distance, q_0 is the amplitude of the vibrational ground state, Q_m is the m-th normal coordinate of the nucleus, Q_{0m} and ω_m are the corresponding amplitude and frequency [22]. One can avoid the explicit use of the differentials of α by considering that I is defined by the difference ($\Delta\alpha$) between the values of α at the two extreme positions of the vibrating atoms; this gives almost the same result (slightly more accurate, in fact) [23]. For a discussion of the convergence of the power series $\alpha(Q)$ and of the contribution from the higher differentials of α the reader is referred to Krushinskii [59].

The relative intensity I_m of the Raman line of frequency $\nu-\omega_m$ (or, more briefly, of the "line ω_m") under normal experimental conditions† is proportional to

$$(\nu-\omega_m)^4(45\,\bar{\alpha}_m'^2+13\,b_m'^2)\,Q_{0m}^2; \qquad (1)$$

where ν is the frequency of the exciting light, $\bar{\alpha}'_m$ and b'_m are the mean value and the anisotropy of the tensor $\frac{\partial\alpha}{\partial Q_m}$. [22] A more detailed treatment can be found in the literature [22,25,26,27].

In the semi-classical theory of Raman scattering [28–30] each Cartesian component (x, y, z) of the differential of α with respect to Q_m is given as the sum of contributions from all the electronic excitation levels e:

$$\alpha'_{xm}=\text{const}\sum_e\left[\frac{f'_{xe}}{\nu_e^2-\nu^2+i\nu\gamma_e}-\frac{2f_{xe}\nu_e\nu'_e}{(\nu_e^2-\nu^2+i\nu\gamma_e)^2}\right], \qquad (2)$$

where the prime denotes a differential with respect to Q_m, f_{xe} is the oscillator strength, measured by the area under the u.v. absorption band for the $O\rightarrow e$ transition (for oriented molecules), ν_e is the frequency of the band maximum, and γ_e is the damping coefficient. Eqn. (2) can be rewritten in terms of the matrix elements of the dipole moment instead of f; in this case a somewhat different relative contribution of the first and the second term in the binomials under the summation sign is obtained, but their sum remains the same [12,16]. We shall consider only the more compact form of the expression, given in Eqn. (2). Without going into details, we note that the intensity (I_m) is given by the square of the modulus of α'_m: in the simplest case, $I_m\simeq\nu^4|\alpha'_{xm}|^2Q_{0m}^2$. In the general case all the Cartesian coordinates have to be considered. Lea's conclusion [31] that the semi-classical theory can deal only with the contribution from a single level and is applicable only to a one-dimensional model is quite unjustified.

Formulae (1) and (2) correspond to steady-state vibration conditions of the electronic oscillator: a definite value of the polarisability of the molecule corresponds to each value of Q_m. These conditions obtain either outside the resonance region or within the resonance region but in the presence of strong damping.

†Standard temperature, irradiation with unpolarised light, disordered orientation of the molecules, and observation at a right angle to the direction of irradiation.

According to Eqn. (2), Raman scattering occurs because both the oscillator strength (f_e) and the frequency of the electronic transition (ν_e) vary during stretching of a chemical bond[28-30]. Placzek's "polarisability theory"[22] takes account only of changes in f_e. The origin of the changes in ν_e is evident from Fig. 3, which shows typical potential energy curves for the ground state, $E_0(q)$, and for an electronically excited state, $E_e(q)$. In formula (2) the values of ν_e and ν'_e correspond to the equilibrium position of the nuclei, $q = q^{(0)}$; in Fig. 3 ν_e is given by the length of the vertical arrow $h\nu_{ev^*}$, and ν'_e by the slope of the curve $E_e(q)$, which depends on the change (Δ) of the equilibrium value of q following electronic excitation. $d\nu_e/dq$ can be as high[30,32] as 10 000–100 000 $cm^{-1}/Å$.

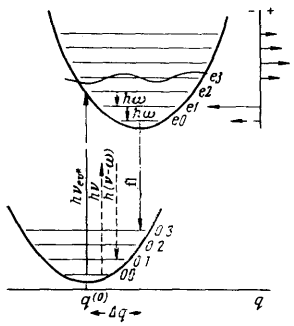


Figure 3. Optical transition model for a diatomic molecule.

From formula (2), and various experimental and theoretical data, we can draw the following conclusions:

1. There is a close relationship between Raman spectra and u.v. absorption spectra. I_m is related to the parameters of the u.v. absorption bands (mainly those in the long-wave region, which are stronger and have a latent or developed vibrational structure corresponding to ω_m, i.e. those with fairly large values of Δ.[16,28-30,33,34] Thus, the intensity is related to the geometry of the molecule in the excited state. The efficiency of particular electronic excitation levels (and the form of the function $I_m(\nu)$) can vary quite significantly for different Raman lines[28,35].

2. When $\nu_e - \nu > 50\,000$ cm^{-1} (aliphatic hydrocarbons under normal Raman excitation conditions), α' and α are practically independent of ν and of ν_e; the intensity of the Raman lines is very low (below the Rayleigh scattering level by a factor of several hundred), and is proportional to $(\nu-\omega)^4$. The Raman lines of cyclohexane[36] are typical of this type of line. The value of α is affected by only a few per cent as a result of nuclear vibrations.

3. When $50\,000 > \nu_e-\nu > 5000$ cm^{-1} (as in the majority of colourless organic compounds) I_m increases rapidly as $\nu_e-\nu$ decreases, both for a series of compounds with decreasing ν_e and for a single compound with increasing ν. On raising the frequency ν of the exciting radiation, the intensity increases faster than by the factor $(\nu-\omega)^4$ of formula (1), since the increase in α' is beginning to have an effect[12,32,33-43]. When several conjugated π-bond systems are present—at least in the case of totally symmetric vibrations—it is not surprising that the second terms in the square brackets of formula (2), containing the factor ν'_e, become dominant[12,32,33,43,44]. Under these conditions the depth of modulation of the molecular polarisability can be as high as 10–20% for small departures from resonance. The polarisability itself is often found to be higher (by 1–10%) than the value expected on the assumption of additivity.

4. When $\nu_e-\nu < 3000$ cm^{-1} (as in coloured compounds) we encounter resonance Raman scattering conditions, first observed in potassium p-nitrophenate[45-47]. This effect is characterised by a very high intensity (though re-absorption can occur under normal experimental conditions). According to Placzek (see Section 25 of Ref. 22), the Raman effect should be replaced by resonance fluorescence when the spectrum is excited within an absorption band. It has been shown[29,30,33], however, that this can only be true at very low damping γ_e (see Section III). Under conditions not very far from resonance it is likely that only one electronic level will be involved, which allows us to ignore the summation over all e in formula (2) and to consider only the contribution from a single electronic level. The imaginary part of α' plays an important role in the resonance region: it determines the depth of modulation of the imaginary part of the polarisability. The achievable depth of modulation of α can be judged by taking p-nitrodiethylaniline as an example: in this compound the difference ($\Delta\alpha$) between the polarisability values for two extreme positions of the vibrating atoms of the nitro group is of the order of 50 $Å^3$ for resonance excitation, whereas the polarisability of the molecule under the same conditions[23] is of the order of 150 $Å^3$.

The resonance denominators in the first and the second term under the summation sign in formula (2) are raised to different powers. Hence, using the function $I(\nu)$, we can identify the cases where either of these terms is predominant: in other words, whether the function $f_e(Q)$ or the function $\nu_e(Q)$ is responsible for the appearance of a Raman spectrum[48], and we can also assess the efficiency of a particular electronic excitation line towards the Raman line under study.

We shall consider the influence on $I(\nu)$ of a single electronic excitation level with large values of Δ_e and ν'_e and a large damping constant ($\gamma_e \gg \omega$) for $f'_e \simeq 0$. Because of the difference in the resonance denominators in the expressions for α'', α', and α,[29,30] the intensity of the overtone increases faster than the intensity of the Raman line of the fundamental as ν increases and the resonance region is approached, and the latter increases faster than the intensity of the Rayleigh line. (Hence, the contribution of Raman scattering to the total scattered intensity increases.) Close to resonance, damping becomes important and the intensity of all the above lines increases more slowly. It reaches a maximum near the maximum of the absorption band, and then begins to fall off (see, for example, Fig. 1 of Ref. 49). We should note that the two maxima in the $I(\nu)$ curve in the region of a single structureless absorption band shown in Fig. 26 of Ref. 25 and Fig. 1 of Ref. 50 are the direct result of the simplifying assumption made[25,50] to describe the electronic level (rectangular well).

A more complete description of the situation is shown in Fig. 4, where the following quantities are plotted: a) the outline of the absorption band $\epsilon(\nu)$; b) the real part of the polarisability Re $\alpha(\nu)$; c) vectors (broken lines) defining the complex polarisability (α) on the complex surfaces for several particular values of the frequency of the incident light (ν). Each of these originates from the position of the corresponding vector on the frequency scale. In this diagram, the projection of the vector on the horizontal axis is the real part of α, and the projection on the vertical axis is the imaginary part of α. Solid-line

arrows denote the complex *derivatives* of α for the same values of ν (the scales of α and α' are in arbitrary units).

The symbol $|\alpha|$ represents the amplitude of vibration of the electronic oscillator, corresponding to a frequency ν for the equilibrium position of the nuclei; $|\alpha + \alpha'|$ relates to one of the extreme positions of the vibrating nuclei; α' (or, more strictly, $\alpha' q_0$) defines the amplitude of the changes in α (occurring with a frequency ω), and the angle between $\vec{\alpha}$ and the horizontal axis is the phase difference between the oscillating field of the light wave and the induced moment $\mu(t)$.

Outside the resonance region, Raman scattering is determined by the amplitude modulation of $\mu(t)$—note that the directions of $\vec{\alpha}$ and $\vec{\alpha}'$ coincide in Fig. 4—and in the resonance region ($\nu \simeq \nu_e$) Raman scattering is determined mainly by phase modulation[23] ($\vec{\alpha}$ and $\vec{\alpha}'$ have different directions). In the latter case, expansion of $\mu(t)$ in a Fourier series gives a whole series of spectral lines $\nu \pm n\omega_m$, where $n = 0, 1, 2\ldots$[51].

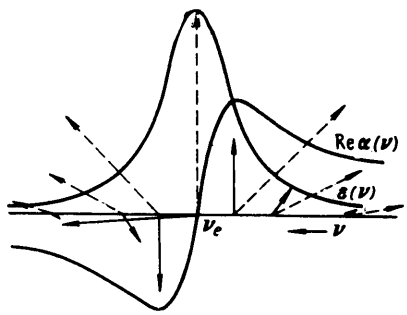


Figure 4. Complex values of α and α' for several values of the frequency ν in the region of the absorption band ($\gamma \gg \omega$, $f_e' \simeq 0$).

When $\nu \simeq \nu_e$, α' is real (see Ref. 25), whereas the contribution of the electronic level to α is imaginary. We must stress the fact that whereas only the real part of α contributes to refraction, both the real and the imaginary part contribute to the intensity of the Raman lines[23]. This is because the nuclear vibrations in different molecules have independent phases.

We have considered the case where ν_e' is the quantity which determines the amplitude of the Raman line. If $\nu_e' = 0$, but $f_e' \neq 0$, the Raman lines for the fundamental and the overtone will have identical $I(\nu)$ functions, coinciding with the corresponding function for the Rayleigh line. Under these conditions, only amplitude modulation of α is possible; as ν is varied, $\vec{\alpha}'$ will vary in the way indicated for $\vec{\alpha}$ in Fig. 4. A proportionality is then found[52] between $\epsilon(\nu)$ and $I(\nu)$, or[41] between $\epsilon(\nu)$ and $I(\nu)/(\nu-\omega)^4$. In general, such a proportionality can be expected for the sum of the intensities of all lines in the scattered spectrum[52]. Experiments on particular compounds with wide absorption bands have shown that $\epsilon(\nu)$ varies in the same sense as $I(\nu)$,[32,33,46] approximate (or exact[53]) proportionality being found in the region of strongest absorption[32].

Most of the existing experimental data on $I(\nu)$, particularly when far from resonance, are difficult to interpret because the u.v. absorption spectra have not been investigated over a sufficiently wide region. This explains also, at least in part, the conflicting conclusions which have been reported on the relative role of the factors f_e' and ν_e' (see Ref. 52–56 and comments in Ref. 57, 58).

A more convincing interpretation of $I(\nu)$ can be obtained in the case of compounds with a strong, isolated, long-wave absorption band. Thus, the intensity of the lines for the nitro group in a series of aromatic nitro compounds has been shown[32] to increase with ν very much faster than expected from f_e'. Even more revealing are the results for the esters of polyene acids (see Section XI), which include a very wide range of $\nu_e - \nu$ values (from 1000 to 30 000 cm^{-1}).[12] In this case it is clear that the factor ν_e' makes a contribution at least an order of magnitude greater than that of f_e' even at $\nu_e - \nu \simeq 10\,000$ cm^{-1}.

It follows from various other results (including fluorescence spectroscopic data) that Δ_e and ν_e' are usually different from zero in totally symmetric vibrations. In diatomic molecules, which have been most thoroughly investigated, it is usually found that $\Delta > 0$ and lies between 0.05 and 0.2 Å; f_e', on the other hand, is relatively small (see discussion in Ref. 59). Lastly, there is a striking agreement between the normal vibrations found in the fine structure of u.v. absorption bands and those found in resonance Raman spectra[11,34].

The form of $I(\nu)$ becomes more complicated if the terms contributed to α' by different electronic levels (or by the two terms for the same level in formula (2)) are of opposite sign[48,57,58]. In such cases, I_m can decrease and even vanish as ν increases over some range of values below resonance, and it can increase quite rapidly beyond that region. However, this behaviour has never been observed in practice; this is in keeping with the view that the contribution from f_e' is small, and can be of either sign, whereas ν_e usually decreases and the polarisability increases when a chemical bond is stretched.

Experimental confirmation has been obtained for the results of the semi-classical theory which predict different $I_m(\nu)$ functions for the different Raman lines of a given compound[35,36], steeper $I_m(\nu)$ functions for small γ,[11] particularly for overtones close to resonance at fairly large values of Δ_e[11,60–62] (but see Ref. 53), and many other effects.

The classical theory of Raman scattering in the simple form discussed above cannot deal with resonance radiation with $\gamma_e < \omega$, i.e. in the presence of vibrational structure in the u. v. absorption band (strictly speaking, when $\gamma_e < 2\nu_e' Q_{0m}$[23]). These conditions are met, for example, in studies of polyacenes, polyenes, and polyynes. Under these conditions the electronic oscillations lag behind the displacement of the vibrating nuclei and cannot reach a steady state. "Forced" and "natural" vibrations of the oscillator become indistinguishable, and beats are produced by the continuous change in the frequency ν_e.[52,63]

In these circumstances the concept of polarisability of a function of nuclear coordinate, used[22] in the "polarisability theory", becomes meaningless. The polarisability can be replaced by a more general function[52], which is time-dependent, similar to the "transfer function" $K(\nu, t)$ used in electronics. This function is determined by solving the equation of motion of the electron, of frequency ν_e, modulated by the motions of the nuclei. Ultimately we obtain a set of Fourier components similar to the polarisability matrix elements used in quantum theory[51]. The most interesting feature of this new variant of the classical theory is its great similarity to the quantum-mechanical theory. In many respects, the general form of the absorption and emission spectra given by both theories is almost the same. It is incorrect to say that the classical theory is concerned with the frequencies of transitions between two continuous potential energy curves for the two electronic levels involved,

whereas the quantum theory deals with transitions between discrete electronic-vibrational sublevels: both theories predict a continuous absorption spectrum for high values of γ and a spectrum with a discrete vibrational structure for $\gamma < \omega$.[51,52]

A further generalisation of the classical theory to include the case of irradiation by a broad-band light source is given in Ref. 63 and 64.

III. QUANTUM THEORY OF RAMAN SCATTERING

The quantum theory of scattering deals with the probability of a change in the vibrational quantum number v, brought about by that part of the energy of the quantum of incident light $h\nu$ which undergoes changes and finally appears as scattered light. The probability of a change in v from 0 to 1 without a change in the electronic state (00 → 01 transition) is defined by the matrix element of the polarisability α_{01}.

It has been shown[23,30,48,52] that the concept of a total wave function ψ for a molecule, expressed as a product of nuclear (u_{ev}) and electronic (φ_e) wave functions, leads to an expression of the type of Eqn. (3):[65]

$$\alpha_{01} = \frac{2}{h}\sum_e \sum_v \frac{\nu_{ev} A_{0v} A_{v1}}{\nu_{ev}^2 - \nu^2 + i\nu\gamma_{ev}} M_{0e}^2 (1 + D_{ev}), \qquad (3)$$

where ν_{ev} is the frequency of the electronic-vibrational transition 00 → ev, in s^{-1}, M_{0e} is the matrix element of the dipole moment of the 0 → e transition, obtained from the electronic wave functions of the ground (0) and the excited (e) state, A_{0v} are the integrals for the combination of the nuclear wave functions of the sublevels 00 and ev, A_{v1} are the integrals for the combination of the sublevels ev and 01, D_{ev} allows for the dependence of M_{0e} on Q. The expressions for α_{00} and the other α_{0n} terms differ from Eqn. (3) only in respect of the subscripts after A. The resonance denominator can be averaged, and the summation with respect to v of the numerators can be replaced by the overlap integrals of u_{00} and $M(Q)u_{01}$, only if $\Delta_e \simeq 0$.

Fig. 3 shows, together with the potential energy curves, the vibrational sublevel systems $0v$ and ev (horizontal lines) which are considered in the quantum theory. $h\nu$ is a quantum of incident light (under resonance excitation conditions) which is transformed into a quantum of scattered light ($h(\nu-\omega)$). The frequency ν_{ev}* corresponds to the maximum of the absorption band of the compound ("Franck–Condon" transition, 00 → ev*). It is clear that the frequencies ν_{ev}, unlike the frequency ν_e which appears in Eqn. (2), cannot be treated as a function of Q (see comments in Ref. 54).

According to Eqn. (3), α_{01} is made up of contributions from several sets of v sublevels in the electronically excited levels. When the individual sublevels merge into a single wide band (for $\gamma_e > \omega$), formula (3) in no way loses its relevance. The contributions from ev sublevels lying above and below ev* have opposite signs (see right-hand side of Fig. 3): when the spectrum is excited far from resonance these contributions effectively cancel out, the summation over v is close to zero,[48] and the Raman line has a very low intensity. As ν approaches the value ν_{e0} the contribution from all the sublevels increases—particularly the lower ones. The compensation of the positive and the negative contributions is progressively lost, and there is a rapid increase in α_{01} and in the line intensity[48].

According to the present theory, Raman scattering results from the presence of a developed (or latent) vibrational structure in the absorption band ($\Delta_e \neq 0$), and also from the dependence of M_{0e} on v (or on Q).

The formulae of the quantum theory are quite different from those of the simple variant of the classical theory. However, when conditions are far from resonance, both sets of formulae predict almost identical intensity values provided that ν_e is taken to be the frequency at the *maximum* of the absorption band[57] (see also Ref. 42 and 66). Under these conditions[22], $\alpha_{01} = \frac{\partial \alpha}{\partial Q} Q_0$. The summation of the ev contributions with different resonance denominators in the quantum mechanical formula (3) corresponds to making allowance for ν_e' in the classical theory; allowing for the small difference in M_{0e} for the different sublevels (or for the parameter D_{ev}) is equivalent[48] to introducing the factor f_e' in formula (2).

Analysis of formula (3) allows us to characterise the secondary resonance radiation of light from various molecules, not involving intermediate transitions in the excited state, for different relative values of γ and ω and for different half-widths (Γ) of the incident light band.

Most of the experimental data on resonance Raman scattering, including those for nitro and nitroso compounds[46,47,49,67,68], relate to the case of $\gamma > \omega > \Gamma$ (excitation by a narrow line, very wide absorption band). Under these conditions resonance scattering differs from non-resonance scattering mainly in the greater line intensity of the former[52]; the relative intensity of the overtones can also be abnormally high.

For somewhat lower values of γ ($\omega > \gamma > \Gamma$ and $\Delta_e \neq 0$), when the absorption band has a developed vibrational structure, one of the characteristics of the normal scattering spectrum tends to be lost (unshifted lines are strongly predominant, and Raman overtones are very weak[69]). This is because a single ev vibrational sublevel makes an overwhelming contribution to the matrix elements of the polarisability α_{0n}. It is possible to find an overtone line with a higher intensity than the fundamental Raman line, and the latter can be stronger than the unshifted scattering line[52]. The secondary radiation acquires some of the features of resonance fluorescence ("transition phenomena of the first kind"). Spectra of this type have been observed in solutions of diphenylpolyenes[11] (Fig. 5) and esters of polyene acids[12] (see discussion in Ref. 27). On going to the conditions $\omega > \Gamma \simeq \gamma$, the similarity between resonance radiation and resonance fluorescence increases: the outline of the bands becomes very similar to the outline of the characteristic lines of the oscillator ("transition spectrum of the second kind"). The situation is illustrated in Fig. 6, and discussed in Ref. 69 and 328.

If γ becomes very small, and comparable with the rotational frequencies ω_{rot} ($\omega_{rot} > \gamma > \Gamma$), different rules apply to the changes in rotational quantum number and the depolarisation of the lines increases. In the first instance, only one rotational sublevel in the ev level can now contribute to α_{0n}, instead of two or three. The increased depolarisation is associated with the onset of "afterglow" under the conditions of molecular rotation. An example of this situation is given[86] by the excitation of the iodine vapour spectrum by the narrow argon laser line, which falls in the region of the fine structure of the I_2 absorption band. On moving still further towards the condition $\omega_{rot} > \Gamma > \gamma$, the predominant spectrum of the secondary radiation should show all the characteristics of resonance fluorescence (including a well developed afterglow).

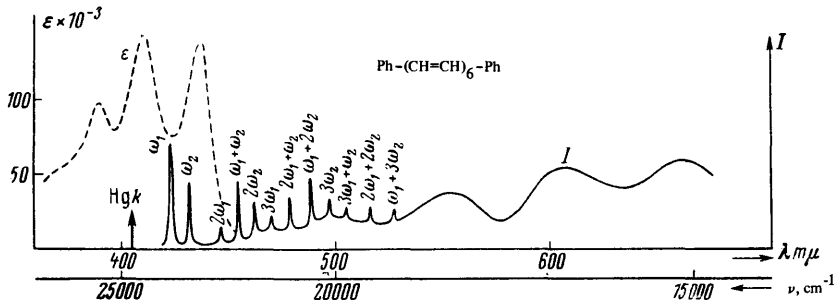


Figure 5. Transition spectrum of the secondary radiation from a solution of diphenyldodecahexaene (full line). The narrow Raman lines are on the left, the fluorescence bands on the right. The exciting Hg*k* line is shown by an arrow. The absorption spectrum is shown by a broken line [11].

On the whole, we may conclude [63] that, depending on the spectral composition of the incident light and on the properties of the oscillator, the secondary radiation can show the typical features of light scattering or of fluorescence, or of an intermediate type of radiation, or alternatively it may combine the properties of one of these types in one part of the spectrum with those of the other type in a different part of the spectrum.

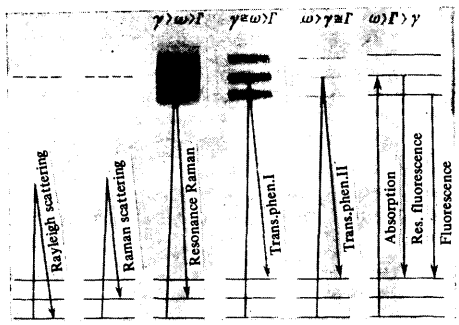


Figure 6. Optical transitions for large and for small damping (γ) of the electronic oscillator (ignoring rotational sublevels). The lower horizontal lines denote the energy of the $\overline{Ov}$ sublevels of the electronic ground state; the upper lines or bands denote the sublevels (ev) of the excited electronic level e.

The theory of Raman scattering summarised above explains [52] the ability of "quenching agents" to eliminate fluorescence with little effect on the intensity of the normally scattered light and of resonance scattering in the same material [37,49]. Normal fluorescence is due to emission from the long-lived, lower vibrational sublevels of ev (arrow labelled fl in Fig. 3), whereas resonance scattering occurs when the sublevels of ev which contribute to α_{on} have a short life-time: these sublevels are, of course, relatively unaffected by quenchers [69].

The simple quantum-mechanical theory and the Kramers–Heisenberg–Weisskopf formula do not extend to resonance scattering by a system with a non-diagonal damping matrix. The off-diagonal elements determine the relationship between the various excitation levels through the field of the radiation: they are considered in models which include quantisation of the light field [70].

IV. EXPERIMENTAL OBSERVATION OF RAMAN RESONANCE SCATTERING SPECTRA

The observation of Raman spectra usually presents no difficulty when the exciting line is not very far removed from the absorption band of the material: data are available for a large number of compounds, including nitroaniline [28,56], Michler's ketone [37,71], nitrostyrene [72], vitamin A, [37] etc. The case of excitation at a relatively large distance from the absorption band ($\nu_e - \nu > > 12\,000$ cm^{-1}) will not be considered here: it includes Harrand's experiments [73] with cinnamaldehyde, chalcone, etc.

Resonance Raman spectra have been obtained for many organic and inorganic compounds of different types and showing both continuous absorption and absorption bands with a fine structure. In addition to the experiments with potassium *p*-nitrophenate mentioned above, spectra have been obtained for solutions of other nitro and nitroso compounds [46,47,42,67,68,74,75], polyenes [11,12,76], derivatives of azobenzene and azonaphthalene [54,75,77,78], pseudoisocyanine [74], Malachite Green [37], $KMnO_4$, [79] iodine [80], and many others (see Ref. 81 for a detailed review). Spectra have also been reported for solids: nitro compounds [5,82], semiconducting crystals [83,84], *F*-centre spectra for alkali halide crystals [85], impurity ions [86], etc. [87] Specially interesting results were obtained with vapours [86]. In all cases the molar intensity of the Raman lines was very high. The largest intensity coefficient was reported for the ester ROOC–(CH=CH)$_7$–COOR: for the 1550 cm^{-1} line it had the value 400×10^6, higher than the strongest acetone line [12] by a factor of 20×10^6. Hence, the line can be observed at concentrations as low as 0.00001% (see Section XI). With lower values of γ the intensity of the secondary emission lines can be even higher (by several orders of magnitude).

Electronic transitions polarised along the chain are characteristic of molecules with an elongated system of conjugated bonds. The corresponding Cartesian component of α_{on} is overwhelmingly dominant under resonance conditions, and hence the degree of depolarisation ρ of most of the Raman lines approaches the value 0.5. [15,67,28,72,88,89] In planar, branched systems ρ can tend towards a different limit of 2/9 (see the results for benzophenone [88]).

Excitation experiments in the absorption region do not always yield positive results [68,37]: this is evidently because the intensity of the line under study includes a contribution from the electronic level, which is to some extent a function of f'_e and ν'_e. When $\nu'_e = 0$, the observation of Raman scattering in the resonance region should be difficult if not impossible, both because the intensity is lower and because of interference from fluorescence bands [27].

Re-absorption of the radiation, even in the region of the strongest absorption bands ($\epsilon > 100\,000$), does not preclude the observation of the stronger Raman lines in sufficiently dilute solutions. An optimum concentration can be defined for each compound [67,75,90]: the formula is given in Ref. 90.

Resonance Raman spectra have provided a broader understanding of the interaction of light with molecules, have led to important results on the relationship between scattering, absorption, and fluorescence spectra, have increased the technological possibilities of Raman spectroscopy, and have given a satisfactory explanation of the effect of conjugation on Raman spectra in systems with different numbers of branches. Perhaps the most interesting results are those on the intensity of resonance Raman spectral lines excited in the region of an absorption band with a developed structure, and in different parts of such a band. These experiments have confirmed the early suggestion [46] that several maxima can appear in $I(\nu)$ under conditions of this type, and also the predictions [33,29] of the life-time of the excited state of a molecule. More details will be found in Section XI.

V. CHARACTERISATION OF MOLECULAR FRAGMENTS IN THE PRESENCE AND IN THE ABSENCE OF CONJUGATION

It is conventional, in studies of intramolecular interactions, to separate the inductive effect from the effects of conjugation (see, for example, Ref. 91 and 92). This procedure, though convenient, is arbitrary to some extent. Different authors use a slightly different interpretation of the inductive effect. In what follows, the term will be used to denote the polarisation of one fragment of a molecule by the electric field produced by another fragment, without redistribution of the electron density in the intervening region.

Conjugation, on the other hand, is the interaction between the electron clouds of two or more chemical bonds. The interaction can be described by a partial *overlapping* and *combination* of their wave functions, set up on the assumption of no interaction (for example, if the conformation of the molecule is unfavourable), with the assistance of the *vacant orbitals* of the fragments. The three aspects which are italicised above differ in their relative importance towards the manifestations of conjugation in different properties of the molecule. Hence, the possibility of establishing simple general correlations is extremely remote.

There is no difference in principle between the various types of conjugation ($\pi-\pi$, $n-\pi$, $\sigma-\pi$, $\sigma-\sigma$). [92,93] They differ only in the form of the overlapping wave functions: the form specifically determines the influence of the mutual orientation of the interacting fragments upon the conjugation. Conjugation increases the number of possible electronic transitions, it has a powerful effect on the optical properties of the molecule, and it leads to a redistribution of the electron density between different groups.

The contribution of the lowest vacant orbitals of the two fragments of the X=C–C=Y system to the filled molecular orbitals is the basis of the so-called "π-electron delocalisation", which amounts to a delocalisation of the valency lines (but in no way characterises the motion of electrons). The redistribution of electron density between non-identical groups of atoms is described in terms of the preferential occupancy of the vacant orbital of one of the fragments. The extent of redistribution is affected by solvation, by the formation of transition complexes, by the application of an external field, by electronic excitation, and during vibration of the atoms. The latter is relevant to the intensity of infrared absorption bands. Depending on the frequency ω and on the extent of overlap of the orbitals of the fragments, the conditions for adiabaticity may or may not be met. The same is true of the frequency of the external field. The aspect which relates to chemical reactions is discussed in Ref. 94.

Conjugation and the redistribution of electron density, under equilibrium configuration and during atomic vibrations, have a significant effect on the frequencies and on the stiffness of chemical bonds. The inductive effect is invoked by many workers, but its role is often exaggerated (see, for example, Sections X and XI and Ref. 95, 96). It is important to note that the relative importance of the various factors which determine the intensity and the frequency of Raman lines is by no means the same: the mutual relationship is far closer in the case of optical properties such as the intensity of Raman lines, polarisability, dispersion, and u.v. absorption spectra (see Sections II and III, and Ref. 97).

The intensity of the Raman lines is one of the molecular parameters most sensitive to conjugation. The reason for this high sensitivity is the presence of higher-power terms in the resonance denominators (see Eqn. (2)). At the same time the intensity (as in the case of the u.v. spectra) is often relatively insensitive to the inductive effect (see Sections IX, X, XI, and also Ref. 95, 96, 98, and particularly Ref. 99 and 100, where reference is made to the Taft constants). When the spectrum is excited close to resonance the intensity is more clearly related to the properties of the particular excited electronic level. Far from resonance and at low field intensities the strength of the Raman lines (like the polarisability) is best described in terms of the characteristics of the electronic ground state.

When the spectra are used to gain information on particular atomic groups in complex molecules it is important to remember that entirely different conditions apply to the localisation of electronic excitation and of normal atomic vibrations. It is not hard to think of a model of the molecule such that electronic excitation is delocalised, but atomic vibration is not, and vice versa. The first case includes molecules in which the fragments involved in conjugation have very different mechanical parameters: for a vibration largely localised in one particular (i-th) bond, $\frac{\partial \alpha}{\partial Q_m} \simeq \frac{\partial \alpha}{\partial q_i}$. But even if the mechanical parameters are similar and the normal vibration can extend to both fragments, we cannot in principle exclude the possibility of

transition to a localised characteristic—from $\frac{\partial \alpha}{\partial Q_m}$ to $\frac{\partial \alpha}{\partial q_i}$ and from $\frac{\partial \nu_e}{\partial Q_m}$ to $\frac{\partial \nu_e}{\partial q_i}$. It should be noted, however, that the partial differentials with respect to q_i (with q_j = const) involve some arbitrariness in the choice of the other internal coordinates $j \neq i$. This is not surprising: the type of deformation of the molecule for a given change of q_i depends on which of the other internal coordinates remain unchanged (see Ref. 101).

As regards the separation of α and also $\frac{\partial \alpha}{\partial q_i}$ into the contributions from particular chemical bonds, which is often attempted, this approach has physical significance only if the bonds are very different, i.e. if local electronic excitation is possible. When the bonds are identical (e.g. in n-alkanes) the electronic excitation levels relate to the whole chain, as in the case of polyenes, but we can formally define the "polarisability" of individual C–C bonds; this procedure gives satisfactory numerical results only when the frequency ν_e is well removed from the frequency ν of the incident light. The increments of α (and also of α') are additive in this case because slight variations in the very high frequencies ν_e and the splitting of the energy levels for different lengths of the –C–C– chain have a negligible effect on the resonance denominators of the expressions for α and α' as compared with (for example) variations in ν_e for the closely spaced levels of polyenes. (Of course, differences in ν_e are also relatively larger in the polyene series [93].) We note that even when identical groups are very weakly conjugated they are included in equal measure in the molecular orbitals.

It should be evident from this example that additivity in the properties of complex molecules (i.e. the ability to describe molecular constants as the sum of increments proper to individual atoms or bonds) is not directly linked, in general, to the location of the actual physical phenomena in which these properties manifest themselves. The concept of delocalisation of the electronic excitation energy and of the atomic vibration energy is quite well defined if specific time constraints are assumed: we have already pointed out that the splitting of levels due to coupling between oscillators is not small, and the "measurement time" and the mean life-time of a state are quite large.

By assuming constant contributions from particular chemical bonds to α and to $\partial\alpha/\partial q$, successful predictions for different molecules can be made, and (if conjugation is absent) good results are obtained for the polarisability and for α'.[102–105] However, the differentials of the polarisability are more sensitive than is α to interactions between groups, and this sets a limit to the usefulness of the additive approach. It is a relatively useless formalism [107] to extend the scheme by taking the differentials $\partial\alpha_j/\partial q_j$ into account, as was done in an attempt to calculate the contribution of an individual bond to the exaltation of refraction [106]. Yet, the most interesting and important cases do involve non-additivity, and one must turn to the values of $\partial\alpha/\partial Q$ and $\partial\alpha/\partial q_i$, and direct measurements of Raman line intensities. Nevertheless, various workers have tried to separate the polarisability parameters of different bonds [54,108].

The possibility of describing the donor–acceptor properties of atomic groups by means of some simple coefficient is very attractive. In practice, however, these properties are strongly dependent on the specific combination of atoms in the group and on their mutual orientation. It is more profitable to consider separately two types of donor–acceptor property: 1) involving an increase and 2) involving a decrease in the multiplicity of the bond between the two interacting groups [109,110]. The OH group must be considered to be a donor group according to its donor–acceptor properties of the first type, and an acceptor group according to its properties of the second type. Depending on its angle of rotation, the amino group can be assigned either to the electron-donating groups of the first type or to the acceptors of the second type. The redistribution of the electron density between the groups depends on the difference between their donor–acceptor properties of the first kind and on the difference between their donor–acceptor properties of the second kind. Thus, every group can be characterised by two coefficients, each of which depends on the angle of rotation of the group.

The possibility of locally characterising the mechanical properties of chemical bonds, even in the absence of conjugation, is very limited. Neither the force constant K_{ii}, nor the interaction coefficient, nor the "independent force constant" (i.e. independent of the choice of the coordinate system for the molecule [101]) can give an accurate characterisation of an individual chemical bond. Strictly speaking, the i-th bond can be characterised only by a set of coefficients (for example, the K_{ij} matrix) which includes off-diagonal coefficients [111,112]. Among these, the most interesting and important are those which describe the interaction of neighbouring chemical bonds: even in paraffin hydrocarbons these coefficients do not vanish [112]. Conjugated double bonds also can interact very significantly [112–115]. All these effects stem from the dependence of the contributions to the inductive effect upon the nuclear coordinate, from the influence of atoms which are not chemically bound, and from conjugation and its associated redistribution of the electron density between the bonds [101]. The off-diagonal coefficients K_{ij} as a rule are much smaller than K_{ii}, but their differences can be as important as the differences in K_{ii} when molecules with different amounts of conjugation are compared. Examples may be quoted ($\omega_{C=O}$ in succinimide, succinic anhydride, etc.) where the difference in frequency between two stretching vibrations is determined mainly by the K_{ij} coefficients. Some data on the relationship between K_{ii}, the order of the chemical bond, and the interatomic distances can be found in the literature [113,116,117].

The classification of molecules into those which do and those which do not show additive behaviour can lead to entirely different results when different properties are studied, and it can depend on the choice of the internal coordinate system for the molecule [111]. Distinguishing between multielectronic and monoelectronic properties of molecules (Dewar [91]) is a somewhat indefinite approach, lacking a concrete physical basis. We prefer to consider the connection between the parameters and electronic excited levels, and also the "time factors" ("measurement time", etc.).

VI. MEASUREMENT OF RAMAN LINE INTENSITIES. SYMBOLS

The intensities of the Raman lines of different compounds are usually determined by reference to the line intensity of a standard compound. The scale which was first proposed took the 313 cm^{-1} line of liquid CCl_4 as 100 units; the intensity of the unknown line was obtained for equimolar proportions of the compound and CCl_4. [17]‡

‡A different scale, in which intensities are referred to unit volume, has been proposed by Sushchinskii [27].

For analytical purposes, the maximum intensity of the line is measured in a spectrometer with a narrow slit, whereas in structural studies the integral intensity is measured [15,28].

The spectra of the unknown and of CCl_4 can be measured separately, under identical conditions (external standard method), or alternatively one can measure the spectrum of a solution in CCl_4 or in another solvent (internal standard method). [117,118] The advantage of the second method is that the results are relatively unaffected by the refractive index of the liquid, which determines the path of the light rays in the cell, and also by light absorption, temperature, stability of the light source, and the specific properties of the medium containing the molecules under study. These advantages are quite important, because reliable corrections for all these factors have not yet been worked out. In practice, of course, most materials are solids of low vapour pressure, and have to be studied in solution irrespectively of the advantages of the two methods, since direct measurements of line intensities on solid samples are not very accurate.

In order to minimise the angular dependence of the intensity, the usual cylindrical cell for the sample is sometimes fitted with a screen which polarises the light at right angles to the cell axis [119]. Under these conditions, the contribution to the intensity from the anisotropic part of the scattering tensor becomes smaller: the term $45\bar{\alpha}'^2 + 13b'^2$ of formula (1) is replaced by $45\bar{\alpha}'^2 + 7b'^2$, and we have the relation [25,120]

$$45\bar{\alpha}'^2 + 13b'^2 = (1+\rho)(45\bar{\alpha}'^2 + 7b'^2) = \frac{6(1+\rho)}{6-7\rho} \cdot 45\bar{\alpha}'^2.$$

However, equally good results are obtained by using simple diaphragms to limit the range of angles of incidence to 90–15°: with this precaution, no modification of formula (1) is necessary. Corrections for self-absorption in the sample can be applied [37,121,122]; other corrections have been discussed in recent monographs [25,27].

The spectra of vapours are very important means of characterising molecules, but they are very difficult to obtain in most cases, and solution spectra have to be examined instead. Under these conditions, the Raman lines of the solvent can be used as internal intensity standards.

For the most accurate measurements of intensity and frequency over a range of materials it is convenient to use a single, well characterised, and preferably inert solvent. Cyclohexane could be quite useful but for its limited solvent power. Solvent effects on the frequencies of various groups in organic compounds have been reported [19,123,124]; these effects have been used in assigning lines [125,126].

In mixtures of aliphatic hydrocarbons, and in a number of other systems, the molar intensity coefficient is independent of concentration [24,67,75], but a significant concentration dependence is found in many cases (in particular, when the degree of association is a function of concentration).

The intensity of lines from the solute usually increases with the refractive index of the solution, even when a correction for convergence of the beam in the cell is applied. On varying the refractive index of the solvent over the range 1.25–1.60 the intensity coefficient for non-resonance excitation is found [132,133] to vary by ±40%. Various approximate formulae for non-specific intermolecular interactions, based on the Onsager model, are derived by Wahl [132]. Association and complex formation introduce additional complications [134–136].

The influence of solvent type is more marked under near-resonance conditions, when the relationship between the shift in the u.v. absorption band and the intensity change becomes unmistakable [15,33,49] (see formula (2); see also Ref. 66, 67, 136–139).

In gases, the line intensity increases with temperature as predicted by theory. In the liquid phase at room temperature the intensity is higher than in the gas phase by a factor of 1.5–3, but on raising the temperature the difference decreases [140]. Most measurements are made at 20–30°: more accurate temperature control is seldom needed in practice.

An attempt has been made to define line intensity constants which are less dependent on measurement conditions: one of these is the absolute intensity [143], or the "activity coefficient" for scattering [144] to use the more recent terminology:

$$A = q_i(45\bar{\alpha}_i'^2 + 7b_i'^2),$$

where q_i is the degeneracy of the nuclear vibrations; in this formula the normal coordinates have the dimensions cm $g^{1/2}$, and the "activity coefficients" are in $cm^4\ g^{-1}$. The latter can be evaluated from experimental data by eliminating the factors $(\nu-\omega_m)^4$ and $[1 - \exp(-\frac{h\omega_m}{kT})]$ and multiplying by ω_m (see formula (1)). The line of the rotational Raman spectrum of the hydrogen molecule ($J = 1 \rightarrow 3$), which has been reliably characterised, has been proposed [145] as a standard for the experimental determination of A. The following results have been obtained: for gaseous CCl_4 $A_{459} = 13.2 \times 10^{-8}$, [146–149] $A_{313} = 4.3 \times 10^{-8}$, [147] whilst for liquid CCl_4 [140,149] $A_{459} = 34 \times 10^{-8}$, $A_{313} = 10.1 \times 10^{-8}\ cm^4\ g^{-1}$. The ratio of the A values for the measured line and for the 459 cm^{-1} line of CCl_4, $S = A_X/A_{459}$, is called [119] the "standard intensity".

The use of coefficients with dimensions $cm^4\ g^{-1}$ ("absolute intensity") to characterise the line intensity has no particular advantage, and introduces unnecessary complications into the interpretation of experimentally observed quantities. Both from the physical and the chemical points of view, it is quite satisfactory to retain the conventional (relative) intensity coefficients, the differentials of the polarisability, or the polarisability matrix elements α_{0n}. For non-resonance excitation the quantity $2\alpha_{01}$ can be identified with the difference between the polarisabilities at the two extreme positions of the nuclei. For a discussion of the "scattering cross-section" the reader is referred to the literature [22,27,150,151].

In the remainder of this review, molar integral intensity coefficients for room temperature are discussed in the text and listed in the Tables. The intensity of the 313 cm^{-1} line of liquid carbon tetrachloride excited by non-polarised light (λ = 4358 Å), and observed at a scattering angle of about 90°, is taken as 100 units; intensity coefficients referred to this standard are denoted by the symbol I^S. The same standard can be used for excitation by frequencies < 22 938 cm^{-1}. The precision of the intensity measurements varies from ±5 to ±20%, depending on the type of apparatus used.

The following I^S values have been reported for liquids: 109 for the 459 cm^{-1} line of CCl_4, [103,118,140,152–157] 43.5 for the 802 line of cyclohexane, [103,158–161] 24 for the 1176 line of benzene [24,28], 12 for the 1031 line of methanol [37,158]; the results are practically identical whether the measurements are made on the pure liquids or on solutions in CCl_4. Excitation by light of much longer wavelength has very little influence on the relative intensity of these lines.

Measurements with a He–Ne laser have also been reported [141,142].

The following symbols are used throughout the remaining Sections: R, Et, Ph for the methyl, ethyl, and phenyl group respectively, Π for a π-bond or a π-bond system. H atoms attached to carbon are omitted in the structural formulae. Q is the normal nuclear coordinate, q is the elongation of the interatomic distance (natural coordinate) in cm or Å.

VII. INTENSITY OF THE RAMAN LINES OF SIMPLE MOLECULES

The differentials $\partial\alpha/\partial q$ (Table 1) are specially interesting as a link between the intensity of Raman lines and other physical constants of the molecule. The best results, obtained for diatomic molecules, justify a number of generalisations about the relationship between line intensity and the nature of the chemical bond. Values of $\partial\alpha/\partial q$ have been obtained also (for relatively simple molecules) by assuming additivity: these need to be interpreted with greater care. The values listed in Table 2 relate to solutions in CCl_4 or to the pure liquids (except for the values for ions, which relate to aqueous solutions). Numbers in brackets are estimates made by analogy or from u. v. spectral data. Values for some other simple molecules and ions can be found in the literature [179,182, 187,188]. Force constant data are tabulated by Müller and Krebs [181].

Table 1. Raman spectra of gases.

Molecule	ω, cm^{-1}	I^s	$\partial\alpha/\partial q$, Å^2	References
H_2	4160	14	1.25	144, 145, 162, 163
D_2	2993	12	1.22	145, 162
N_2	2330	6.5	1.7	162–164
O_2	1555	10	1.45	162–164
HCl	2886	—	1.0	164
HBr	2558	—	1.2	164
CO	2155	6.5	1.5	162, 163
$H_3C{-}CH_3$	994	—	1.0	165–168
$H_2C{=}CH_2$	1623	~12	1.9	165, 166, 169
$HC{\equiv}CH$	1973	35	3.15	165, 166, 168
CO_2	~1340	19	1.95	162–164, 169, 170
CH_4	2914	32	1.05	147, 166, 168
CD_4	2108	25	1.0	167, 171
CT_4	1738	(22)	1.0	167
CR_4	734	20	1.15	166, 172, 173
CF_4	908	7	0.97	147, 171, 173
CCl_4	459	42	2.1	147, 168, 174
SiR_4	596	~65	~1.9	172
SiF_4	800	7	0.88	171
GeR_4	559	~100	~2.2	172
SnR_4	507	~200	~3.0	172, 176
PbR_4	459	~300	~3.2	172, 176
NH_3	3334	~ 20	~1.0	162
H_2S	2614	32	~1.3	162
SF_6	775	20	1.23	171
SeF_6	710	32	1.47	171
TeF_6	697	31	1.4	171
AlkOH	3640	~7	1.0	132, 175, 177

It has been known for many years [22] that purely ionic bonds cannot contribute to Raman scattering, because the electron clouds of the cation and the anion are mutually independent. (Ion pairs in close contact can give very weak lines.) Bonds with a weakly covalent character give low-intensity lines because [189] the potential energy curve of the excited electronic level has a small curvature. In the simplest cases, this small curvature can be ascribed to the fact that the energy difference between the bonding and the antibonding molecular orbital is relatively unaffected by bond stretching, since it is due to a difference in the field surrounding the two atoms rather than to overlapping atomic orbitals.

Table 2. Raman spectra of compounds in the liquid phase (column headings as in Table 1).

Molecule	ω, cm^{-1}	I^s	$\partial\alpha/\partial q$, Å^2	References
CCl_4	313	100	—	—
	459	109	3.35	see Section VI
CBr_4	267	360	6.0	178, 179
CI_4	178	(2000)	—	180, 181
$SiCl_4$	424	130	3.3	130, 178, 182
$GeCl_4$	396	290	4.8	130, 178, 182, 183
$SnCl_4$	367	540	6.1	178, 179, 182, 184
$SnBr_4$	221	1540	10.6	184, 178
SnI_4	149	(20000)	(~35)	180
$TiCl_4$	387	920	8.4	178, 182
PCl_3	510	170	—	182
PCl_5	394	800	—	182
$SbCl_3$	360	450	—	182
$BiCl_3$	288	520	—	182
$ZnCl_4''$	282	40	1.45	179
$ZnBr_4''$	172	170	3.0	179
$HgCl_4''$	267	260	3.5	179
$HgBr_4''$	166	1500	8.5	179
CO_3''	1060	21	1.75	182, 185
NO_3'	1040	62	2.8	182, 185
PO_4'''	935	22	1.55	182, 185
AsO_4'''	820	70	2.35	182
SO_4''	980	45	2.3	182, 185
ClO_3'	934	50	2.3	185
ClO_4'	935	73	2.9	185
IO_4'	797	226	4.6	185
$(N{=}N{=}N)'$	1343	47	—	186
CN'	2079	18	2.9	187

$\partial\alpha/\partial q_i$ is practically unaffected by isotopic substitution. The intensity can vary a little because of the difference in the amplitudes q_i, but this effect is negligible except in the case of the hydrogen isotopes. The intensity and $\partial\alpha/\partial q$ both increase with the multiplicity of the bond; for carbon–carbon bonds $\partial\alpha/\partial q$ is proportional to the order of the bond [166]. For C–H bonds (but not for C–C bonds [187]) $\partial\alpha/\partial q$ is independent of hybridisation of the atomic orbitals of the C atoms [132,166]. The intensity of the lines of MX_n molecules increases very considerably [182] as the valency of the M atom increases. Differences in $\partial\alpha/\partial q$ for chemical bonds of a given type in molecules and ions are generally small; no obvious trend has yet been detected. The intensity and $\partial\alpha/\partial q$ increase with the atomic weight of the atoms involved in bond formation: if σ-bonds are compared, this effect may be explained by the decrease in the energy of the $\sigma \rightarrow \sigma^*$ electronic excitation.

Some of the above aspects are implicit in the approximate empirical formula for MX_4 molecules given by Pauling for $\partial\alpha/\partial q$ in terms of the percentage covalency (p) of the bond, defined by the electronegativity difference between M and X:

$$\partial\alpha/\partial q \sim p(z_M + z_X),$$

where z is the atomic number of the element [178].

Lippincott [190] gives a relationship between the differential $\partial\alpha/\partial q$ and the multiplicity (n) of the bond, the electronegativity of the atoms in the given valency state (χ_1 and χ_2), and the number of filled s, p, d, and f shells. In his model, the potential in the region of each nucleus is described by a δ-function. A local molecular orbital independent of other bonds is obtained by a linear combination of the wave functions of the two atomic orbitals. In Long and Plane's interpretation [179], this model gives the differential of the bond polarisability in the form

$$\frac{\partial\bar{\alpha}}{\partial q} = \frac{\sqrt[4]{\chi_1\chi_2}}{\sqrt{z_1 z_2}} \frac{\sigma n q_0^3}{a_0};$$

where $\sigma = \exp[-\frac{1}{4}(\chi_1 - \chi_2)^2]$ defines the covalent character of the bond, q_0 is the equilibrium distance between the atoms, a_0 is the Bohr radius of the first orbital of the H atom, and z is the effective charge on the nucleus. Lippincott and Nagarajan [190] replace z by empirical functions of the filling of the s, p, d, and f shells; values of x/z are tabulated for all atoms [191]. This formula often leads to serious discrepancies with experiment. It has been used [179] to evaluate bond multiplicity in a large number of molecules and ions.

Non-empirical and semi-empirical quantum-mechanical methods have been used a number of times to calculate $\partial\alpha/\partial q$ for the hydrogen molecule: in general, the results were satisfactory [325]. Further discussion of the application of the additivity hypothesis to polyatomic molecules can be found in Ref. 173, 189, 192–194.

VIII. INTENSITY OF THE CHARACTERISTIC LINES OF THE MOST IMPORTANT ATOMIC GROUPS

Among the most interesting Raman lines of organic compounds are those which characterise the quasi-local stretching vibrations of atomic groups (for example, carbonyl, hydroxyl, cyano, nitro). Their position in the spectrum (Table 3) is relatively independent of the structure of the rest of the molecule. In the few cases where such a relationship was observed, it was ascribed to the effect of conjugation or some other form of intramolecular interaction upon the rigidity of the chemical bond.

The intensity of the Raman lines for quasi-local vibrations usually varies very little among the members of a homologous series. Thus, in the alk-1-ene series from pentene to tetradecene (and also in the cycloolefins [197,276]) the intensity of the so-called "C=C vibration" line lies between 30 and 35 units; similar information exists for other hydrocarbons [24,161,198]. Replacement of the H atoms on the C=C double bond by alkyl groups increases $I_{C=C}$ (to 50 in the case of tetraalkylethylenes); [195,198] calculations by the additive scheme suggest that this effect may arise from the contribution of the new bonds to the differential $\partial\alpha/\partial Q$, without any change in the parameters of the double bond ($\partial\alpha/\partial Q_{C=C}$). [105] It should be noted, however, that the u. v. absorption bands of alk-1-enes and tetramethylethylene appear in different positions, and this effect alone may explain an increase in intensity by 25–30%; thus, the simple "additivity scheme" is not fully adequate in this case. A similar state of affairs is found on going from toluene to hexamethylbenzene (line at ~ 1600 cm^{-1}). [199] A small increase in $I_{C=O}$ and $I_{C\equiv N}$ is observed experimentally when comparing the first with the subsequent members of the ketone [100,200,201] and the cyanide [99,138] homologous series.

Various workers [98,35,202–209] have reported an approximate proportionality between characteristic line intensities and the number of like atomic groups when the latter are separated by one or more carbon atoms with sp^3 hybridisation, or by the group SiR_2 or SnR_2§. Molecules with different bridging groups often show significant deviations from additivity (see Section XIV).

Table 3.

Group X chemical bonds		Alk—X			Ph—X		I^S(PhX)/I^S(AlkX)	References
		ω	I^S	$\partial\alpha/\partial q$	ω	I^S		
—CH_3		~2900	~40	1.4	~2900	50	~1.2	24, 167
	C—C	~1000	—	1.2	—	—	—	166–168
—SiR_2H	Si—H	2118	90	2.1	2122	105	1.2	132, 211, 212, 326
—SH	S—H	2586	52	2.0	2586	75	1.4	132, 213, 214
—CH_2·S·CH_2—	C—S—C	680	50	—	—	—	—	214
—CH_2F	C—F	875	15	1.2	—	—	—	
—CH_2Cl	C—Cl	655	50	2.5	—	—	—	215–217
—CH_2Br	C—Br	557	100	4	—	—	—	215, 216
—CH_2I	C—I	497	200	7	—	—	—	215, 216
—CH(NH)CH_2		~1300	26	—	1300	39	1.5	218
—CH_2—SnR_3		507	~350	—	480+ +510	~1000	~3	176, 202
—SOR	S=O	1048	48	—	—	—	—	§ 142 [sic]
—SO_2R		1135	~100	—	1160	~80	~0.8	219
—$CONR_2$	C=O	1655	21	—	1636	60	3	98, 100, 126, 220–222
—COOEt	C=O	1745	14	—	1725	100	7	15, 98, 100, 220, 223
—COR	C=O	1719	14	2.2	1690	160	11	15, 37, 98, 104, 220
—COCl	C=O	1803	12	2.5	1770	170	14	35, 100, 104, 200, 220
—COBr	C=O	1812	14	—	1780	200	14	200, 220
—COH	C=O	1729	13	2.9	1704	230	18	35, 98, 100, 104, 220
—Ph	C=C	1605	26	2.2	1600	~700	~13	107, 220, 224
—CH=CH_2	C=C	1642	30	3	1631	340	11	15, 37, 196, 225–227
—C≡CH	C≡C	2118	75	5	2110	400	5,3	37, 99, 129, 228–230
—CN	C≡N	2254	32	4.2	2231	330	10	35, 138, 187, 231–234
—NO_2		1380	35	—	1348	700	20	28, 35, 72, 235

Table 3 lists relative intensity data for the characteristic stretching vibration lines of various atomic groups in molecules of the RX type (mostly, EtX), and also the corresponding $\partial\alpha/\partial q$ differentials; the frequency ω is obtained from data for solutions in CCl_4 (except the starred values, which relate to different solvents); the values of I^S and $\partial\alpha/\partial q$ refer to the pure liquids or to solutions in CCl_4. We note that α' and I^S increase with the multiplicity of the bond, with the atomic weight of the bond-forming atom in X, and also with the intensity of the u. v. absorption band of RX and with its approach towards the visible end of the u.v. spectrum.

The reader is referred to the original literature for an account of the characteristic lines of various types of branched hydrocarbon chain and of cyclic molecules [27,205,208–210].

§The total intensity of the line splitting components should give a more exact proportionality.

IX. EFFECT OF SUBSTITUENTS ON THE SPECTRA OF COMPOUNDS WITH C–C π-BOND SYSTEMS

A large amount of data is available on the effect of various substituents on $I_{C=C}$ and on the differentials $\partial\alpha/\partial q_{C=C}$,[15,16,207,220,226,227,236] on $I_{C\equiv N}$,[99,138,187,235] on $I_{C=O}$,[15,98,100,200,220] and on $I_{C\equiv C}$.[99,203,204,228,230] Among these substituents, the phenyl group has attracted particular interest (see last three columns of Table 3). Table 4, on the other hand, gives some indication of the influence of other groups upon the benzene ring. It was pointed out in 1953 [71] that substituents usually have a stronger influence on the intensity of lines for conjugated bonds than on the intensity of lines for isolated multiple bonds. These relationships are discussed in Section X.

Table 4.

Group X in PhX	I^s_{1600}	EMR, cm^3	u.v.spectra in heptane λ_1	λ_2	λ_3	σ_{para}	References
—H	35	0	2540 *0.2*	2030 *7.5*	1830 *50*	0	107, 24
—D	35	0	—	—	—	0	107
—SO_2R	28	—	2640 *1.0*	2150 *8.0*	1890 *57*	0.8	107, 223
—F	28	—0.05	2600 *1.1*	2030 *7.3*	1820 *48*	0	107
—OCOR	36	—	2650 *0.3*	2100 *8.0*	1860 *53*	—	71, 98, 222, 226
—Cl	35	0.15	2610 *0.3*	2140 *8.0*	1890 *61*	0.2	107, 224
—Br	37	0.10	2610 *0.3*	2150 *8.0*	1925 *35*	0.2	107, 224
—OH	38	0.28	2700 *2.0*	2110 *6.5*	1890 *56*	—0.3	107, 153, 224
—R	39	0.25	2620 *0.3*	2050 *8.0*	1880 *53*	—0.15	17, 37, 24, 220
—NR_2H^+	~40	—	—	—	—	—	237
—CH_2CN	40	—	2570 *0.2*	2060 *7.0*	—	0	232
—C—C—Ph	40	—	2600 *0.5*	2080 *20*	1880 *100*	—0.1	220
—C—NR_2	41	—	2580 *0.2*	2070 *12*	1880 *60*	—	220
—I	42	0.15	2600 *0.7*	2300 *12.5*	1940 *28*	0.3	107, 224
—SiR_3	45	0.1	2580 *0.3*	2130 *9.0*	1900 *70*	—	238
—OR	50	0.35	2715 *2.0*	2165 8.5	1920 *50*	0.25	153, 220, 222
—O—C=C	58	—	2720 *1.2*	—	—	—	15, 223, 225, 239
	65	—	—	—	—	—	240, 241
—C—SiR_3	80	0.5	2680 *0.4*	2240 *8.5*	1950 *52*	—	238
—$B(OBu)_2$	80	—	2670 *0.8*	2200 *10.6*	1910 *47*	—	242
—NEt—COR	80	—	—	2380 *5.5*	2000 *20*	—	126
—CCl_3	80	0.35	2690 *0.6*	2250 *7.0*	1925 *43*	0.45	71
—SH	90	0.5	2760 *0.7*	2350 *8.5*	2030 *22*	0.45	107, 213, 214
	90	0.3	2640 *0.5*	2190 *8.6*	1930 *52*	—0.1	218, 223, 241, 243
	95	—	2600 *0.2*	2170 *8.0*	1900 *32*	—0.1	218
—SR	100	0.8	2800 *1.5*	2540 *9.8*	2030 *14*	0	107, 223
—NH_2	100	0.95	2850 *1.6*	2350 *8.0*	1980 *30*	—0.5	34, 153, 220, 224
—CH_2I	110	—	2720 *2.2*	2340 *10*	2020 *23*	—	232
—$CONR_2$	110	—	2700 *0.6*	2250 *10*	1890 *35*	—	98, 220, 222
	112	0.45	2750 *1.0*	2340 *12*	1990 *30*	—0.3	218
—COOEt	135	0.8	2770 *1.0*	2290 *12*	—	0.6	98, 222
—CN	150	1.0	2700 *0.65*	2230 *13*	1920 *52*	0.8	34, 37, 153, 222
—NR_2	170	1.5	2960 *2.0*	2500 *14*	2010 *22*	—0.6	107, 218, 220, 224
—C≡C	180	1.4	2750 *0.4*	2380 *16*	1990 *33*	—	37, 228, 229
—COR	190	0.9	2800 *1.0*	2385 *13*	1980 *31*	0.7	37, 98, 153, 220
—NO_2	200	0.9	2810 *1.5*	2520 *9*	1980 *18*	1.0	45, 37, 107, 224
—CHO	200	1.1	2810 *1.3*	2410 *14*	1980 *27*	0.8	98, 107, 222
—NHCHO	210	—	2780 *1.4*	2390 *13.5*	1980 *24*	0	107, 126
—C=C	250	1.4	2820 *0.75*	2460 *14*	2040 *23*	0	45, 37, 224–226
—COCl	250	—	—	—	—	—	98, 222
—COBr	300	—	—	—	—	—	98
—NH·Ph	350	—	—	2830 *20*	2070 *21*	—	220, 224
—Ph	370	2.0	—	2470 *18*	2000 *38*	0	37, 107, 220, 224
—C—HgI	(1000)	—	—	2590 *16*	1990 *30*		244
—C=C—C=C	1100	3.0	—	2750 *26*	2200 *12*		107
—C=C—PCl_2	~1300	—	—	—	—		226
—C=C—COOEt	1400	3.1	—	2720 *21*	2160 *17*		107
—C=C—CHO	1800	3.3	—	2790 *25*	2200 *13*		37, 107
—C=C—NO_2	3200	4.0	—	3000 *17*	2290 *10*		107
—$(C=C)_2$—COR	(5000)	(5)	—	3100 *33*	2350 *8*		

Note. H atoms attached to carbon have been omitted in the formulae. The symbols are defined in Section VI.

Very similar mutual effects are observed in PhX compounds and in compounds with various CC π-bond systems (or one such bond) in place of the Ph group. Hence, many of the conclusions obtained from studies of PhX compounds are capable (in principle) of being generalised. However, compounds in which the π-bond system has degenerate donor–acceptor properties exhibit some additional specific features.

Table 4 lists some intensity coefficients for the characteristic line of the benzene ring, lying in the region 1570–1610 cm^{-1}. Alkylbenzenes have two closely spaced lines (the vibration modes are given in Fig. 1 of Ref. 107). The higher-frequency line is associated with a symmetric vibration of the ring (though some workers have erroneously assigned it to an antisymmetric vibration). Its intensity (but not its frequency) is extremely sensitive to the effect of substituents [125,153]. In the presence of conjugation this line is the predominant one, and the second line of the doublet makes a negligible contribution to the experimentally observed total intensity (designated I_{1600} in the Table). The spectra of PhX contain also a characteristic line at ~ 1000 cm^{-1}, whose intensity is far less sensitive to the nature of X: the ratio I_{1600}/I_{1000} can therefore be used to study conjugation with the benzene ring [153]. Table 4 gives only the I_{1600} values; for molecules containing two benzene rings the quoted value is $0.5 \cdot I_{1600}$.

The third column of Table 4 lists the exaltation of molecular refraction (EMR) for λ = 5893 Å arising from the interaction [107] between Ph and X. The next three columns give the wave lengths of the u. v. absorption band maxima which are genetically related to the benzene bands (λ given in Å for solutions in heptane). The figures in italics are $\epsilon/1000$ values, where ε is the molar decimal absorption coefficient at the band maximum [244]. The penultimate column contains the Hammett σ_{para} constants. Literature references to the quoted I_{1600} values are given in the last column of Table 4.

Table 4 summarises the properties of compounds with different types of substituent X. No direct effect on the spectrum is observed, whether the group is an electron donor, an electron acceptor, or neutral, and also whether or not it contains multiple bonds, unshared electron pairs, or heavy atoms. In each of this types, both "active" and "inactive" groups can be found. There is only one important general rule: large values of I_{1600} and EMR are usually associated with u. v. absorption bands which are both strong and close to the visible region of the spectrum. As a rule, substituents of all types tend to increase λ, I_{1600}, and EMR. [107,244] However, the deviations from additivity of the dipole moments (Δμ, see Ref. 107) are not all of the same sign: hence some justification exists for classifying substituents into electropositive and electronegative types.

When the substituent X in PhX compounds contains CC π-bond systems, both Δμ and σ are almost zero, and yet the deviations from additivity in the optical properties are large. On the other hand, substituents which favour the inductive effect (F, NR_2H^+, SO_2R) have finite (and often large) values of σ and Δμ, but their effect on the optical properties is very slight. Cases have been reported of substituents affecting some optical properties in the positive sense and others in the negative sense. Hence we may conclude that simple (linear) correlations between the optical parameters, the electronegativity of the groups X, and the σ constants are unlikely to exist [107] (see also Sections V and XII).

It is evident, from the general properties of PhX compounds, that the intensity of the Raman lines due to

π-bonds is extremely sensitive to conjugation ($\pi-\pi$, $n-\pi$, $\sigma-\pi$) and relatively insensitive to the inductive effect. Donor–acceptor interactions (leading to a redistribution of the electron density between parts of the molecule), to which anomalies in the dipole moment are ascribed, have only an indirect influence on the optical properties.

A consideration of the system of energy levels or MO energies for models of the type PhX or C=C–X makes it obvious that the absorption bands can be shifted towards longer waves by electronegative, electropositive, or even neutral X substituents in the presence of conjugation [244]. The potential well model of the electron indicates that the electronic levels should move closer together when the well is made wider. Thus, any addition to the molecule which increases the length of the chain (at least, in the absence of steric hindrance) should induce a bathochromic shift of the u. v. absorption bands [93] and increase the intensity of the Raman lines.

Table 5. Spectroscopic evidence for the effect of substituents X (shown above the numerical entries) in compounds of type PhX (I_{1600}, figures on the left) and C=C–C—X ($I_{C=C}$, figures on the right); the differences in $\omega_{C=C}$ between the compounds C=C–C–X and C=C–Alk are shown in heavy type.

I	II	III	IV	V	VI	VII
Li (50) (>1000) — —		 (100) 35 **–7**	CR_3 39 30 **0**	NR_2 170 30 **0**	OR 50 (30) **–2**	F 27 (25) **8**
Na — — — — **~–100**	MgAll — — — — **–40**	$AlAll_2$ — — — — **–12**	SiR_3 40 54 **–12**	PR_2 (80) — — **–7**	SR 100 (40) **–5**	Cl 35 35 **0**
	ZnAll — — — — **–20**		GeR_3 (40) 100 **–12**	AsR_2 (60) (100) **–10**	SeR (100) (70) — —	Br 37 55 **–5**
			SnR_3 (50) 260 **–17**	$SbAll_2$ — — — — **–13**	TeAll — — — — **~–10**	I 42 90 **–14**
	HgCl — — 700 **–15**					

Note. Numbers in brackets are tentative estimates of I from u.v. spectral data. "All" denotes the allyl group. This Table was assembled from data in Refs. 232, 245, 246, and also 176.

We shall now consider in detail the influence of substituents not containing multiple bonds. Table 5 gives some indication, in spite of the scarcity of experimental data, of the way in which the position of the substituent atom Z in the Periodic Table affects its influence on a π-bond or a π-bond system (denoted by the letter П) in groupings such as П–Z and П–CH_2–Z.

When Z is directly adjacent to П, the largest effect on the optical properties and on the rigidity of the bonds is produced by the atoms N and S ($n-\pi$ conjugation). The P atom has a significant effect, and its orbitals (including $3d$) contribute to the delocalised MO [226] (see also Ref. 227). The influence of the boron atom is ascribed [242] to the contribution from its vacant $2p$ orbital.

There is a shortage of data on the influence of Z on the force constants (rigidity) of π-bonds in П–Z systems, and indirect arguments are unreliable in this context, because of the appreciable contribution from the C–Z bond to the "π-bond vibration". Increased rigidity in П–Z systems (as compared with П–R systems) has been observed on a number of occasions (fluoro derivatives, chloro-anhydrides); decreased rigidity of C=C, C≡N, C≡C has been found to be induced by the atoms Si, Ge, Sn, [207] O, [247], S, [225,247] and N. [248] The effect of the Si, Ge, and Sn atoms arises mainly from $\pi-d$ conjugation involving the vacant d orbital of the Z atoms, [204,207,249] or from the inductive effect [207,250]; the effect of halogens is mainly inductive [200], that of the N, S, and O atoms is the result of $n-\pi$ conjugation.

Compounds in which Z is from Groups I–III of the Periodic Table have not been investigated in detail, but a significant lowering of the frequency of multiple bonds has been observed (see for example Ref. 251). This effect may be partly due to a decrease in the rigidity of the bond. However, calculated values of $K_{C\equiv N}$ for RHgCN and $Hg(CN)_2$ did not differ appreciably from those for RCN. [252]

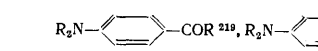
Decreased rigidity of a π-bond is often accompanied by an increased intensity of the Raman line. In spite of the contribution of the ordinary C–Z bond to the "π-bond vibration" of the П–Z system in antiphase (provided the mass of Z is not too low), [225] the intensity of the π-bond line is usually increased by substituents [204]. This is closely bound up with the fact that conjugation in its various forms tends to shift the u. v. bands towards the longer-wave end of the spectrum (see above). According to Jones [253], the values of I^S_{CN} for mercuric cyanide and $H_2C(CN)_2$ are practically identical.

X. $n-\pi$ CONJUGATION

The influence of atoms having a labile unshared electron pair on the rigidity of π-bonds and on the optical properties of the compound is usually ascribed to $n-\pi$ conjugation involving a π^* orbital, but some workers have invoked the inductive effect [248]. The rigidity of the π-bond is decreased by a small amount (3–5%), and the rigidity of the C–Z bond is increased by a large amount (up to 30%): [248] this is usually interpreted as some measure of double bond character. It is interesting to note [248] that the off-diagonal force coefficient which determines the interaction between the C–Z and the π-bond has a positive influence in this case: this means that stretching of the π-bond is accompanied by a shortening of the C–Z bond and vice versa [101].

The tendency of the Z atom to $n-\pi$ conjugation depends [254] on the p character of the orbitals of the unshared pair: the most favourable conditions correspond to overlapping of the n and π orbitals in systems.

Compounds with a well developed $n-\pi$ conjugation show a bathochromic shift of the u. v. absorption bands and an increased intensity of the Raman lines for the multiple bond. Some of these systems are listed below in increasing order of effect of $n-\pi$ conjugation on intensity:

AlkO—COR [15,220], AlkO—C=C [15,226,239,255],
AlkS—C=C [225],
R_2N—COR [126,220], R_2N—C≡N [138], Alk_2N—C=C [126],


There is no increase in the intensity of the C=O line for the first member of this series, but in the last two

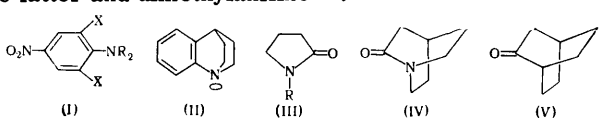
members I_{CO} and I_{NO_2} are increased by over a factor of ten as a result of the presence of the amino group. The fact that the amino group increases I_{CO} by only a factor of 1.5 in R_2NCOR and by a much greater amount in *p*-aminoacetophenone is explained by the relative positions of the strong u. v. absorption bands of these compounds (in the far u. v. for the former, and much nearer the visible region for the latter). The shift of a closely spaced band is reflected more strongly by the resonance denominator in the expression for the intensity than is the shift of a more remote band. (We note, however, that the λ shift produced by an amino group becomes somewhat smaller when the chain of conjugated bonds is extended still further.)

The redistribution of electron density between substituents, which affects the dipole moment of the molecule and $\omega_{C=O}$, is determined by different considerations. The effect is strongest if R_2N and COR are immediately adjacent, somewhat weaker if these two groups are separated by a benzene ring, and weaker still when a more complex system of CC π-bonds is interposed. These observations are easily explained by considering the systems of energy levels of the main fragments of the molecule and the combination of their wave functions with formation of delocalised MO and new electronic transitions (see, for example, Fig. 6 in Ref. 244).

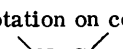
In the light of the above, it is not surprising that the anomalies in optical properties of the molecule $PhCONR_2$ are associated mainly with interactions in the Ph–CO system, whereas the dipole moment anomalies relate to the system $CONR_2$.[220]

On spectral and dipole moment evidence[219,231] conjugation with the SO_2 group is very weak in sulphonamides; the observed shortening of the N–S bond is ascribed[256] to local interaction with the vacant S *d*-orbital.

The $n-\pi$ conjugation conditions are very dependent on the angle of rotation of the conjugated groups. In unsubstituted dimethylaniline, when steric hindrance is negligible, the two methyl groups are symmetrically disposed on one side of the plane of the benzene ring, and the wave function of the unshared pair of electrons effectively overlaps the *p* orbital of the carbon atom. The same is true of 4-nitrodimethylaniline. In the 2,6-disubstituted derivatives of dimethylaniline and 4-nitrodimethylaniline (I), the NR_2 group is rotated through an angle which does not favour conjugation (the direction R...R forms a fairly large angle with the plane of the ring). The influence of NR_2 on the benzene ring and on the nitro group becomes much weaker[257]. In benzoquinuclidine (II) the wave function of the unshared electron pair (shown by an oval symbol in formula (II)) is "cleaved" by the nodal plane of the *p* orbitals of the ring into two equivalent zones: the $n-\pi$ overlap integral therefore vanishes, the unshared pair is practically immobilised, and the nitrogen atom has almost no effect on the optical properties. Nevertheless, benzoquinuclidine is very different in basicity from quinuclidine, and is intermediate in basic strength between the latter and dimethylaniline[258].

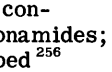


(I) (II) (III) (IV) (V)

Some data on the effect of angular rotation on conjugation effects are available for the system  . Thus, *N*-methylpyrrolidone (III) has an almost planar b Od system, and shows distinct conjugation effects: the C=O frequency is lower than in cyclopentanone by 55 cm^{-1}, and $I_{C=O}$ is slightly higher[126]. On the other hand, in quinuclidone (IV), where the overlap integral of the *n* and π* orbitals is zero, $\omega_{C=O}$ is actually much greater than in bicyclo-(2,2,2)-octan-2-one (V).[259] We note that an increase in $\omega_{C=O}$ is usually observed on introducing electronegative substituents (for example, in RCOCl). These results suggest that a given group can behave either electropositively or electronegatively depending on its angle of rotation. It is interesting to note that the basicity of quinuclidone (IV) is much lower than that of quinuclidine[259] in spite of the unfavourable geometry of the N–C=O system from the point of view of conjugation.

Not surprisingly, all evidence of $n-\pi$ conjugation in aromatic amines disappears on forming salts: see the data for $PhNR_2$ and $PhNR_2H^+$ in Table 4.

In Π–OR and Π–SR systems, n,π conjugation is most evident when the fragments are in the same plane. Conjugation is very weak in non-planar mesityl compounds. It has been pointed out[260] that the sulphur atom has both donor properties (resulting from the unshared electron pair) and acceptor properties (resulting from the vacant 3*d* orbital). In some systems the donor properties are almost absent, but the acceptor properties persist because π-*d* overlapping is retained.

Some data suggest a difference in conjugation behaviour between *s-cis* and *s-trans* isomers. Simple vinyl ethers have mainly the *s-trans* form, and they show low $\omega_{C=C}$ and $K_{C=C}$ values and high $I_{C=C}$ values as a result of the influenee of OAlk;[15,226,255] no such behaviour is found with compounds of the type  .[261] In the analogous cyclic compound of sulphur both $\omega_{C=C}$ and $I_{C=C}$ are modified[261], but in every case they are lower than in the open-chain molecule[225].

XI. $\pi-\pi$ CONJUGATION

Molecules with alternating multiple and single bonds usually show a small decrease (0–20%) in the rigidity of the multiple bonds and a more substantial increase (up to 30%) in the rigidity of the intervening single bonds, which has been ascribed partly to atomic orbital hybridisation phenomena and partly to some measure of double bond character (nitrobenzene[262], diacetylene[263,264], glyoxal, acrolein[114], butadiene[113,265], and to a lesser extent diacyanogen[113]). However, different authors have obtained entirely different quantitative results. Some workers conclude that the off-diagonal force coefficient which characterises the interaction of the two π-bonds has a large, negative value[113,114,263]; this implies that the stretching of one π-bond induces an additional force field in the other π-bond, tending to elongate it[101].

The clearest evidence of $\pi-\pi$ conjugation comes from the increased intensity of Raman lines—in particular, the lines associated with stretching vibrations of conjugated multiple bonds. There are some early qualitative reports[266] of unusually strong lines from C=C and C=O double bonds in the presence of conjugation. Quantitative measurements of $I_{C=O}$ in acetophenone and benzophenone[215], I_{NO_2} in nitrobenzene, nitronaphthalene, and nitroaniline, $I_{C\equiv N}$ in benzonitrile and vinyl cyanide, and $I_{C=C}$ in styrene, vinyl cyanide, acrylates, butadiene, and hexatriene[15,28] have shown that a high intensity is characteristic of coplanar systems of alternating multiple and single bonds[28]. An unusually strong C≡C line has been

observed in phenylacetylene [37,229]. When an electronegative group (CN, NO_2, COR) is combined with a system of CC π-bonds, the lines of both fragments show an abnormally high intensity (particularly those of the electronegative group).[28] Oxalates [200,220], and vinyl and phenyl sulphones [219,227,231], show no enhancement of refraction or of Raman line intensity in spite of the non-additivity of the dipole moments in phenyl sulphones (see Tables 3 and 4).

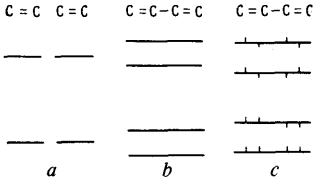


Figure 7. Filled and vacant π orbitals in the C=C-C=C system: *a*) in the absence of conjugation, *b*) and *c*) in the presence of conjugation for two extreme positions of the C atom ("symmetric C=C vibration"). The vertical strokes in diagram *c* denote the sign of the AO contributions.

Experiment has shown that $I_{C=C}$ is approximately 10 times higher in butadiene than in mono-olefins, and 10 times higher still in the triene [15]. Further increase in the number of conjugated double bonds makes the intensity progressively higher [12].

Studies of the absorption spectra and of $I(\nu)$ lead to the conclusion that the difference in ν_e between butadiene and mono-olefins is sufficient to account for a four-fold increase in intensity. If account is taken also of differences in oscillator strength, in the amplitude of the natural coordinates, and in the anisotropy, the ten-fold increase in intensity in butadiene can be explained by applying formula (2).[35] It should be noted that after the transition of an electron to the lowest vacant orbital (π_3^*), the equilibrium value of q_{C-C} should decrease a little and that of $q_{C=C}$ should increase (though by less than in the corresponding $\pi \rightarrow \pi^*$ transition in mono-olefins). The same conclusion follows from the fact that the wave function of π_3^* has nodal points in the region of the double bonds but not in that of the intervening single bond (see Fig. 7). Thus, the equilibrium value of the normal nuclear coordinate for the "stretching symmetric vibration of the C=C bonds" should by changed by electronic excitation, and $\partial\nu_e/\partial Q$ should be non-zero. Systems with different numbers of conjugated double bonds are discussed in detail in Ref. 12.

Facer and Thompson [129] have proposed a formula for the intensity, including terms which allow specifically for the effect of "mesomerism" and for the shift in ν_e, and appear to be unsoundly based.

Calculations for the butadiene molecule by various MMO variants give a π order of between 0.15 and 0.5 for the central C–C bond and between 0.8 and 0.95 for the double bonds. It is stated [267,268] that the alternation of bond orders and force constants [113,269] found in butadiene is retained almost unchanged in the polyene chain. The decrease in the "C=C vibration" frequency with increase of chain length is due to a slightly increased contribution from ordinary bond vibrations, not to a change in $K_{C=C}$.

An increase in the length of the polyene chain has little effect on $\omega_{C=O}$, but it leads to a rapid increase of $I_{C=C}$ and $I_{C=O}$, with extremely high values under resonance conditions, when the frequency of the exciting light (22 938 cm^{-1}) is in the region of the absorption band. With still further increase in chain length the band in the electronic absorption spectra is shifted towards the red and the intensity of the Raman lines (as expected from theory) begins to fall off. The very high intensity obtained by resonance excitation of the spectra of polyenes is due to the relatively small damping constants ($\gamma < \omega$!).

Table 6.

n	$\omega_{C=C}$	$I^s_{C=C}$	$\omega_{C=O}$	$I^s_{C=O}$	ν_e
0	—	——	1760	40	——
1	1664	300	1733	350	48 100
2	1643	5000	1726	800	38 500
3	1620	30000	1721	1800	33 700
4	1597	150000	1717	6000	30 400
5	1572	$1.2 \cdot 10^6$	——	——	28 200
6	1562	$17 \cdot 10^6$	——	——	26 300
7	1550	$400 \cdot 10^6$	——	——	24 800
8	1540	$200 \cdot 10^6$	——	——	23 300
10	(1500)	$(50 \cdot 10^6)$	——	——	(20 500)

Data [12,76] for the C=C and C=O lines of the series of compounds EtOOC–$(CH{=}CH)_n$–COOEt (in acetone) are set out in Table 6 together with the position of the main u. v. absorption band (ν_e, cm^{-1}). Values shown in brackets are tentative extrapolations. The u. v. spectra are shown in Fig. 8.

Vol'kenshtein and Yazykova [270] have tried to calculate $I_{C=C}$ for a molecule with conjugated C=C bonds by using the metal model (π-electron approximation); the symmetric vibration of the double bonds was modelled by simply changing the length of the potential well, leading to a change in ν_e. Savin [271,272] applied the π-electron approximation to a single electronic transition, and described the changes in ν_e induced by the vibration of the atoms in the chain by taking account of the coefficients for the type of vibration. In the final variant, the potential was assumed uniform along the chain. Good qualitative agreement with experiment was obtained in both these investigations.

It should be possible to calculate α and α' under non-resonance conditions for any (not too complex) molecule, irrespectively of whether the additive scheme or the free-electron model is applicable, by computing the electronic energy levels and transition probabilities for all the electrons, and their interactions. Of course, calculations based on MMO LCAO are not very precise, but they have some predictive value.

Contradictory views have been expressed on the role of the inductive effect in molecules with conjugated multiple bonds. The question can be answered with greater confidence by comparing molecules in which the mutual orientation of the fragments is different, for example in the "benzene ring–nitro group" system. The deviations from additivity in the optical properties, dipole moments, and many other parameters of the planar, unsubstituted nitrobenzene molecule (the angle of rotation of the nitro group about the C–N bond is $\theta = 0°$) are quite substantial.

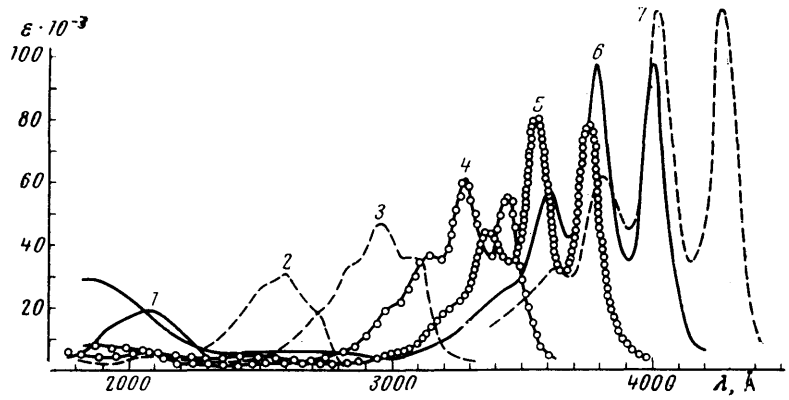


Figure 8. Absorption spectra of heptane solutions of EtOOC-(CH=CH)$_n$-COOEt. The value of n is shown on the curves.

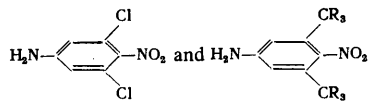
The introduction of substituents in the *ortho*-position increases the value of θ to a greater or lesser extent, which can be calculated from the force field. We express[95] the potential energy of the molecule as

$$U = U_0 + U_u + U_{def} + U_\theta,$$

where U_0 is the energy of the planar molecule in the presence of conjugation and in the absence of steric hindrance, U_u is the energy expended against forces acting between unbound atoms, U_{def} is the energy needed to deform the bond angles, and U_θ is the conjugation energy. U_{def} can be determined by introducing angular force constants, U_u can be determined by means of the Lennard-Jones potential function. A knowledge of the van der Waals radii is not sufficient, because the atoms are not rigid spheres; furthermore, the potential is influenced by any excess of positive or negative charge on the atoms. This explains, at least in part, why Cl, Cl *ortho*-substituents affect the rotation of the nitro group more strongly than CH_3, CH_3, whereas the converse is true of the rotation of the NR_2 group[95].

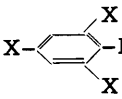
Table 7 shows a set of data[95,273] for derivatives of nitrobenzene: a) the difference between the nitro-group frequency of the given compound and that of unsubstituted nitrobenzene (1348 cm^{-1}, in benzene solution); b) the intensity I^S of the line of the nitro group (in benzene solution); c) the absorption coefficient at 2500 Å (in heptane solution); d) the deviation from additivity in the dipole moment; e) the estimated angular rotation θ of the nitro group. The figure in brackets is a tentative estimate.

It is evident from Table 7 that the mutual effect of Ph and NO_2 is almost completely suppressed when the angle θ is large. The interaction between the nitro group and substituents in the *para*-position also has been shown to be weakened, for example in the molecules[257,274]



In the latter compound the calculated rotation[274] is $\theta = 80°$, and the intensity of the first strong u. v. band is decreased by a factor of 20. It is interesting to note that the rotated nitro group retains some of its effect on the basicity of the amino group: this is ascribed[274] to the fact that the inductive effect persists even though conjugation has disappeared.

Thus, we may conclude that, in spite of the large polarity of the nitro group, the inductive effect has a negligible influence on the rigidity of chemical bonds in aromatic nitro compounds, on their dipole moments, or on their optical properties, but a large effect persists on the rate constants of chemical reactions with an ionic mechanism.

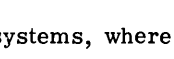
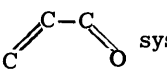
Table 7. Spectra of X-  -NO$_2$ compounds in nitropropane.

Group X	$\Delta\omega$, cm^{-1}	I^S	ϵ_{2500}	$\Delta\mu$	θ
H	0	700	9600	0.8	0
CH_3	17	250	1900	0.4	55°
Cl	14	50	1300	0.1	70°
Br	10	50	3500	0.1	—
$C(CH_3)_3$	29	(40)	800	—	75°
$PrNO_2$	36	35	—	0	—

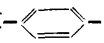
On going from trichloronitrobenzene to tribromonitrobenzene, I_{NO_2} decreases (as expected), but ϵ_{2500} increases. It is evident that the "benzene ring–bromine atom" system is beginning to dominate the u. v. spectra, so that any information regarding conjugation with the nitro group is lost. It is equally difficult to detect disturbance of the conjugation from $\Delta\omega$ values, because the frequency is affected by the mass of the halogen atoms. The I^S values are not significantly affected[95] by these factors. Egorov and coworkers[196] have published some interesting results on non-planar fluoro-derivatives of stilbene.

Planar *s-trans* and *s-cis* systems show some interesting differences in the conjugation of their double bonds. The intensity of the C=C lines in diene systems of the *s-trans* type is approximately twice as high as that of the *s-cis* systems[275,276]. This is partly due to the lower contribution of anisotropy in α' to the observed intensity

in the *s-cis* systems. The force field is very different in the two cases, as shown by the relative frequencies of the two forms of stretching vibrations of the double bonds: in *s-cis* dienes (as opposed to *s-trans* dienes) the antisymmetric vibration has the higher frequency, possibly as a result of differences in the off-diagonal force coefficients. The effect of conformation on $I_{C=C}$ is particularly strong in trienes [275].

In  systems, where the C=C and C=O vibrations are fairly well separated [114,277], $I_{C=O}$ is large [15,98,278], and in  systems $I_{C=C}$ is large [277]. In the latter case the vibrations are less localised: the higher frequency, and more substantial contribution from the C=O bond, are assigned [279] to the "anti-phase" vibration of the double bonds, and hence the intensity of the line is small.

Many papers have been published on cyclic diene systems [44,234,275,276,280,281] and on open-chain diene compounds [205,281,282].

XII. CONJUGATION IN X–  –Y MOLECULES

In compounds of the X–C_6H_4–Y type, changes in the frequency ($\Delta\omega_Y$) of the quasi-local vibration of the group Y under the influence of X can be used directly as an approximate criterion of changes in the rigidity of the chemical bond, which can be as high as 10%. Difference of 2–4 cm^{-1} in ω_Y are significant in this respect. The effect on the frequency and on the stiffness of the bonds is most marked for a pair of substituents one of which is an electron donor of the first type in Section V, the other an acceptor (a *k*-acceptor and a *k*-donor in the writer's terminology [109,110]); the effect is smallest when the two substituents are of the same type. The same is true of the deviations in additivity of the dipole moments and of the specific features of Hammett's σ constants. These effects are illustrated in Fig. 9, which shows the correlations between $\Delta\omega_Y$ and the donor–acceptor properties of the group X, characterised by the deviations from additivity in the dipole moments of the molecules PhX. (A positive value of $\Delta\mu$ corresponds to a shift of the electron density from X towards Ph.) The data for NO_2 and NH_2 are arithmetic means of $\Delta\omega^S$ and $\Delta\omega^{as}$. These curves were drawn from measurements of ω in CCl_4. [225,231,283,284] The influence of X on ω_Y is sometimes enhanced by solvation in more "active" solvents, and is less marked when the molecules are isolated as in vapours (see the data for *p*-nitroaniline and other similar compounds [124]).

As regards the influence of substituents on the intensity, the conjugation conditions (in particular, the number of conjugated bonds) are the determining factor for the Raman lines of multiple bonds. Thus, the vinyl group (or a whole system of CC π-bonds) in position X has a negligible effect on the frequency of the lines for the double bonds of the group Y (a few cm^{-1}), but it has a powerful effect on their intensity, which may change by a factor of 1000. This phenomenon is closely bound up with the effect on ν_e.

The large decrease in the frequency ν_e of the first u. v. absorption band when X and Y groups of different types are combined can be explained by considering the energetics of the orbitals of the fragments and of the MO of the X–П–Y system (see Fig. 6 of Ref. 224). A decrease in ν_e has a direct effect on I_Y, but changes in ν_e' and f_e' are also important (see Section II). Some calculations can be found in Ref. 235.

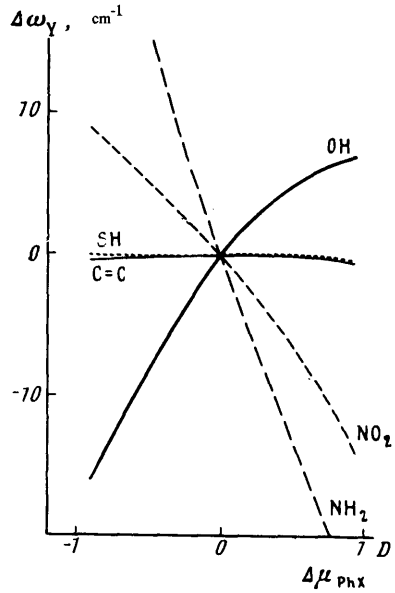
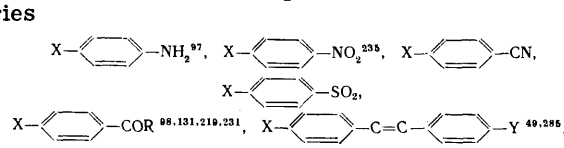


Figure 9. Change in ω_Y under the influence of the group X in X– –Y compounds; the group Y is specified on the curves.

A comparison of various parameters of molecules in the series



has revealed a number of correlations between deviations from additivity in the dipole moments, the $\Delta\omega_Y$ values, and the Hammett constants (σ) for the group X. [97] On the other hand, approximate correlations have been observed between the various manifestations of the mutual effect of the groups X and Y in different optical properties [235]: the greater the deviations from additivity in the effects of X and Y on the u. v. spectra, the more prevalent are large values of I_Y (at least for the lines from double and triple bonds), exaltation of molecular refraction, and dispersion of the refractive index. However, various attempts to establish simple relationships between pairs of the above parameters (e.g. between I_Y and σ_X) have been successful only over a very limited range of compounds (see Ref. 66 and 138).

XIII. CONJUGATION WITH A THREE-MEMBERED RING

Compounds containing a three-membered ring show certain similarities with olefins in chemical properties (for example, in addition reactions involving ring-opening).

Their physical and chemical properties suggest interaction between the three-membered ring and systems of double bonds. A significant increase in the intensity of the Raman lines due to multiple bonds and to the three-membered ring has been observed in cyclopropylketones [201], vinylcyclopropane [286,287], phenylcyclopropane [218,243], and glycidates [127]. It is interesting to note that in *p*-dicyclopropylbenzene the intensity of the line for the benzene ring (I_{1600}) is even higher than in phenylcyclopropane: the behaviour is similar to that of a conjugated chain [243].

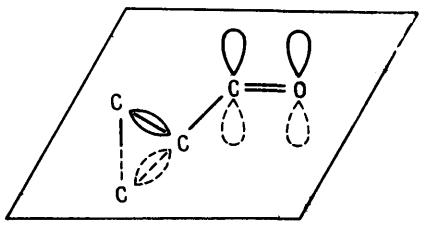
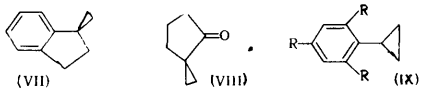


Figure 10. Disposition of the orbitals in the spirocyclopropancyclopentanone ("three-membered ring–double bond") system.

Phenylcyclopropane and *C*-phenylethyleneimine are intermediate between toluene and styrene (see Table 4) in their I_{1600} value and in their u. v. spectra. This evidence of conjugation has been ascribed [288] to hybridisation of the AO of the carbon atom in the three-membered ring, leading to some measure of sp^2 character. The valency electrons which form the ring are assumed to have some π-electron character. The configuration in which the three-membered ring and the π-bond system are in mutually perpendicular planes (see Fig. 10) is most conducive to conjugation [286]: this is found, for example, in spirocyclopropanindane (VII) [288] and spiro-cyclopropancyclopentanone (VIII). [289] In mesitylcyclopropane (IX) the optimum conformation from the point of view of conjugation cannot be achieved, and in this compound I_{1600} is hardly greater than in mesitylene, which suggests that conjugation is almost entirely absent [287].



(VII) (VIII) (IX)

If the C<(C)(C) plane in isopropylbenzene is perpendicular to the plane of the benzene ring, the highest filled σ-orbital of C<(C)(C) can overlap the *p*-orbital of the C_{ar} atom. However, significant perturbation and combination of the wave functions is precluded by the large difference in energy of the orbitals of the two fragments. These effects can occur, however, with the cyclopropyl group, because of the lower energy of its $\sigma \rightarrow \sigma^*$ transition.

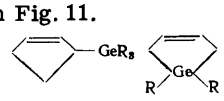
According to Bent [290], the electronegative nitrogen atom in *C*-phenylethyleneimine should enhance the *p*-character of the bonds in the three-membered ring. This is not confirmed by an analysis [218] of Raman line intensity data.

In *N*-phenylethyleneimine, Ph–N<(C)(C), I_{1600} is determined mainly by n,π conjugation, which is controlled by the rotation of the three-membered ring. This compound differs from phenylcyclopropane in having the two C atoms on the same side of the Ph plane. I_{1600} for *N*-phenylethyleneimine is lower than the value for $PhNR_2$ by almost a factor of two: this is ascribed [218] to the more pronounced *s* character of the unshared electron pair of the nitrogen atom.

XIV. SYSTEMS WITH A BRIDGING ATOM (Π–M–Z). σ–π CONJUGATION

Systems of bonds with a bridging atom are extremely interesting. They include some radicals found in the majority of organic compounds. In a number of systems of the type $\Pi-CH_2-Z$ and similar systems with different bridging groups (Π–M–Z), the influence of Z is as strong as in the system Π–Z (see Tables 4 and 5). [232,244] However, the special features of the effect are different in the two cases. Thus, the N atom of the amino group has a strong effect on the spectra in Π–Z systems, but practically none in $\Pi-CH_2-Z$ systems, whereas the opposite is true of the Hg atom. The presence of an unshared electron pair in Z, and the polarity of the substituent, have only a minor significance in systems with a methylene bridge, but heavy atoms have an important effect [220,232,291]: within a given period of the Periodic Table, the effect of Z on the Raman and u. v. spectra of $Ph-C-ZR_n$, $C{=}C-C-ZR_n$, and other similar systems increases somewhat on going from right to left [291]. This tendency is most marked with compounds which include a *k*-acceptor group—for example, $ROC-CH_2-ZR_n$—since conditions are then favourable for donor–acceptor interactions and the rigidity of the double bond is decreased more substantially [245] (see Table 5, which lists $\omega C{=}C$ and I_{1600} for the corresponding allyl and benzyl compounds).

It has been shown [291] that as the atomic weight of the atom Z increases (within a given sub-group of the Periodic Table) the effect of the substituent on the optical properties of $\Pi-CH_2-Z$ systems increases and the frequencies ν_e of the u.v. $\pi-\pi^*$ bands decrease. Under these conditions molecules which are known to be non-planar (as opposed to π,π conjugated systems) show the largest deviations from additivity. Thus, compound (X) has Raman and u.v. spectra [245,291,292] ($I^S_{C=C} = 160$ [292]) very different from those of cyclopentene ($I^S_{C=C} = 28$), whereas molecule (XI) which has an almost planar ring is similar to cyclopentene ($I^S_{C=C} = 25$ for (XI) [292]). The u.v. spectra of these compounds are shown in Fig. 11.



(X) (XI)

These spectra repudiate [292] the view [293,294] that the key role is played by the overlap of two *p*-orbitals of the C atoms adjacent to the double bond with a *d*-orbital of the Si atom (C=C–Si) or with Hg orbitals in systems like C=C–C–Z.

None of the above experimental results, including those concerning angular dependences, in any way conflicts with the view that $\sigma-\pi$ conjugation can be ascribed

to the overlap of the wave functions of the double-bond π-orbitals with the two-centre orbital of the C–Z σ-bond (or the multi-centre orbital of the C–Z group). When the σ-bond is in the plane of the π-bond system (in the nodal plane of the p-orbitals) the overlap vanishes, and when it is at right angles to this plane the overlap is a maximum. On the other hand, when the orbital energies of conjugated π and σ bonds are similar, and the latter bond includes a heavy atom Z, combination of the wave functions is favoured [291]. Several authors have studied the system R_3Si-CH_2-COR, and have variously concluded that the most important effect is the inductive effect [250], the interaction between the unshared electron pair of the oxygen atom and the vacant Si–orbital [295], or the presence of a resonance structure of the type $Si^+C=C-O^-$ (see Ref. 250). In benzyltin and other similar compounds the inductive effect [296] or p_π-d_π conjugation [293,327] are the most important.

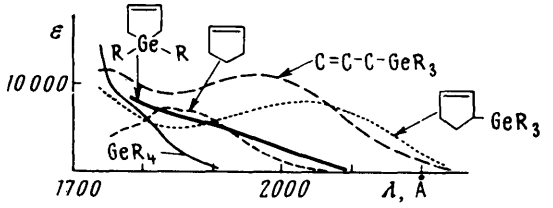
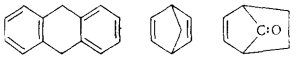


Figure 11. U. v. absorption spectra (in heptane solution).

The virtual absence of σ-π conjugation effects in ordinary open-chain organic molecules containing C, H, N, O, and Cl atoms is due to the high energy of the $\sigma \rightarrow \sigma^*$ transition and therefore to the small contribution of the C–Z σ-bond to the highest filled and the lowest vacant MO; the low conjugation energy ($< kT$) does not allow the bonds to take up the orientation most favourable to conjugation.

In systems of the type $\Pi-CH_2-\Pi'$ the deviations from additivity in the Raman (and also the u.v.) spectra are quite insignificant. (The systems which have been investigated include Ph–C–Ph, Ph–C–C–Ph, [220] Ph–C–C=C, [161] C=C–C–C=C, [281] Ph–C–CN, [232] and limonene [15].) However, when the fragments have some well defined orientations (as in tripticene, where the planes of the three benzene rings are at 120° to each other) the first u.v. absorption band has a high intensity [297]. In dihydroanthracene (XII), norbornadiene (XIII), and other similar compounds the anomalies are not very marked; it has been suggested [298] that in these molecules the two electronic oscillators are weakly coupled.



(XII) (XIII) (XIV)

Most workers consider that the most important effect in this type of molecule is the overlap of the p orbitals of the two nearest carbon atoms from different fragments. Depending on the orientation of these AO, large differences in the perturbation of the electronic levels are possible. Thus, in system (XIV) the p orbital of the C atom of the carbonyl group partly overlaps the C=C π orbital (but not the π^*, which has a nodal point in the middle of the double bond). On the other hand, the AO of the unshared electron pair of the oxygen atom overlaps the π^* orbital (though to a very small extent). Hence, the energies of the various electronic transitions are affected in different ways. In the spirene molecules the systems of double bonds lie in mutually perpendicular planes, but some interaction can nevertheless take place; in spiro-nonatetraene we expect interaction between the highest filled and also the highest vacant orbitals of the fragments [299] (see Fig. 12).

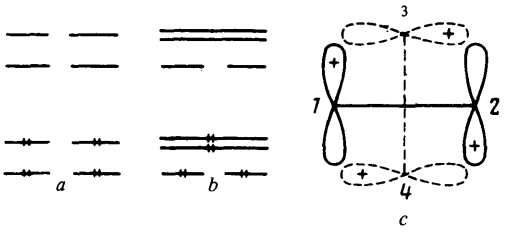
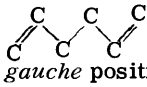


Figure 12. Energy of the π orbitals in the system: *a*) for the two separate fragments; *b*) in the presence of interaction between the fragments; *c*) p orbitals of the carbon atoms *1*, *2*, *3*, *4* (the observer is looking along the symmetry axis *4*). The signs correspond to the upper filled MO.

Cookson [300] considers a system of bonds of the type  . If the central C–C bond is in the *gauche* position with respect to each of the double bonds, its σ orbital is assumed to overlap the π orbitals of the two C=C bonds, with the possibility of splitting of the π electron levels and "σ-coupled π-electron transitions". Under these conditions the C–C σ bond takes practically no part in the electronic transition but it allows delocalisation of the transition.

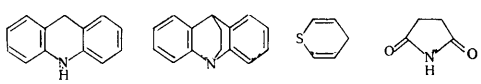
In molecules of the type $X-CH_2-Y$ where X is an electron-donor group of the first type (see Section V) and Y is an electron-acceptor group of the second type, donor-acceptor interaction can occur with increase in the multiplicity of the X–C bond and a corresponding decrease in the multiplicity of the C–Y bond. Under favourable conditions, ions can be formed: $(X^+=CH_2) + Y^-$ (for example, $R_2N^+-CH_2-Cl \rightarrow (R_2N^+=CH_2) + Cl^-$, see Ref. 301). The combination of a donor group of the second type and an acceptor group of the first type gives, in the extreme case, the structure $X^+ + (CH_2=Y^-)$, as in $K^+ + (CH_2=NO_2^-)$.

The cyano group has weaker acceptor properties of the second type than has the Cl group; accordingly, the molecule $R_2N.CH_2.CN$ does not form ions similar to those suggested above for the chloro compound. However, their Raman spectra show a fairly large drop in ω_{CN} and in the rigidity of the C≡N bond; the characteristic absorption band of the amino group at 1900–2000 Å ($n \rightarrow \sigma^*$ transition) is considerably weakened, and the basicity of the amino group is decreased. All these effects are consistent with the participation of the unshared electron pair of the amino group in conjugation of the type described above [232]. Similarly, it has been shown [302] that the N–C bond is shortened and the C–CN bond in lengthened even when the orbitals of the triple bond and of the unshared

pair on the amino nitrogen cannot overlap. The influence of the amino group on ω_{CN} is much smaller in compounds of the type p-$R_2N-C_6H_4-CH_2-CN$ than in R_2N-CH_2-CN, but it can be detected [303]. The effect is entirely absent in the analogous carbonyl compounds, showing that COR has a very low capacity as an electron acceptor [232].

Data on compounds with -O-, -S-, and -NH- bridges and fragmentary and sometimes contradictory. Most of the work has been done on compounds of the Ph-M-Ph type, particularly diphenylamine, which in spite of lack of coplanarity, and some "competition" between the two electron acceptors, shows clear evidence of non-additivity: I_{1600} is higher than in aniline by a factor of 6 (see Ref. 220, where the u.v. spectra are also given). According to the u.v. spectra, the same deviations from additivity are found in acridan (XV). The Raman spectra indicate considerable interaction between the double bonds in N-vinylpyrrolidone. Acetanilide has very strong lines from the C=O group and the benzene ring; in the spectrum of Ph.NR.COR the symptoms of n-π conjugation with the carbonyl group are enhanced, and those of conjugation with the benzene ring are suppressed. This observation has prompted the conclusion that the angular rotation of the NRCOR group relative to the Ph plane is increased, and that conjugation in the N-C=O system is strengthened [126].

The main contribution to interaction in nitrogen-bridge systems comes from the unshared electron pair of the nitrogen atom, which is determined by the relative orientation of the fragments (see above). In the dibenzoquinuclidine molecule (XVI) the unshared pair is immobile, and as a result of this the spectroscopic evidence of interaction between the benzene rings and of n-π conjugation is almost totally absent [304].



(XV) (XVI) (XVII) (XVIII)

Π-S-Π′ systems have smaller deviations from additivity than the corresponding nitrogen-bridge systems. Nevertheless, $I_{C=C}$ for C=C-S-C=C was found to be at least double the value expected on the assumption of full additivity [223,280]. Judging from the u.v. spectra [305], the effect should be even greater in thiopyran (XVII). However, the carbonyl group in the C=C-S-COR system is found [306] to have a negligible effect on $I_{C=C}$. No deviations from additivity can be detected in Π-SO_2-Π′ systems [223,280].

Even smaller anomalies were found in compounds with an oxygen bridge [15,223,226,239,307,308]. $I_{C=C}$, $I_{C=O}$, and I_{1600} are slightly enhanced in compounds with the bond systems C=C-O-COR, Ph-O-C=C, and C=C-O-C=C, and an even more significant effect is found in $C_6H_5.C_6H_4.O.C=C$. In the presence of steric hindrance (for example, in mesityl vinyl ether) interaction effects are almost zero [223,239].

One interesting feature of the spectra of Π-M-Π′ systems with -O-, -S-, and -N- bridges is the fact that the frequencies of the π bonds adjacent to the bridging atom are higher (by 5-10 cm^{-1}) than the corresponding frequencies for Π-M-R and R-M-Π′ compounds; this effect may be due to the increased rigidity of the bonds, and possibly also to the contribution of off-diagonal elements [112,115]. In succinimide (XVIII) and in succinic anhydride the off-diagonal element corresponding to the interaction of the two C=O groups is fairly large; this element is related to the interaction conditions in the two n-π conjugated systems [112].

Very little is known about the influence of heavy atoms in Π-O-Z, Π-S-Z, and Π-NH-Z systems. In systems of this type, n-π conjugation favour a planar conformation, which in turn excludes σ-π conjugation. Mesityl compounds are known to be non-planar, with large θ angles, but no other information is available. Heavy atoms have been shown [291] to have less effect on the u.v. spectrum of the benzene ring in Ph-O-Z systems than in $Ph-CH_2-Z$ systems. The u.v. spectra of $Ph-NH-SiR_3$ do not differ significantly from those of Ph-NH-R. [309] Various workers [187,188,283] have found that the mercury atom in the -Hg-CN system has little influence on $\partial\alpha/\partial q$ for the C≡N bond, but its effect is quite large in -Hg-S-CN systems.

No departures from additivity have been observed in $Si(HC=CH_2)_4$, $Si(C\equiv CH)_4$, and other similar Si compounds, but the influence of heavy atoms through the Si bridge is apparently even greater than through the methylene bridge. Whereas the u.v. spectra of PhR and $PhSiR_3$ are practically identical, the compound $Ph.SiR_2.SiR_3$ (where the Si-Si bond is believed to form a large angle with the plane of the benzene ring) shows a large bathochromic shift of the u.v. band [93], which increases with the length of the chain of silicon atoms [310]. Since such chains give rise to a distinct closing-up of the electronic levels, conditions become favourable for combination of the wave functions of Ph and the substituent [93] (Sakurai and Kumada [311] have termed this a dative p_π-d_π bond). Non-additivity is particularly evident in the spectra of $Ph-(SiR_2)_n-Ph$ when n is large [312]; it is independent of the parity of n and indicative of direct participation of the orbitals of the bridging atoms in the conjugation. The interaction of benzene rings through the Sn-Sn group has been ascribed [313] to participation of the d orbitals of Sn, and in a similar way [242] the interaction through a boron atom has been ascribed to the participation of the $2p$ boron orbital.

The mutual influence of atomic groups in molecules of the type Π-M-Π′ and Π-M-Z is far from being fully understood, and widely different hypotheses and conclusions are currently being discussed. From the whole of the available data it would appear that interaction can take place by a number of different paths, including: 1) direct overlap of the orbitals of relatively close atoms of the groups Π and Π′ or of the orbitals of Π and Z; 2) participation of the orbitals of bridging atoms in the delocalised orbitals of the molecule (for example, in systems with σ-π or π-σ-π conjugation); 3) non-additive interactions (e.g. in n-π conjugation) in Π-M and M-Π′ systems, particularly as regards the population of the AO of the bridge.

Spectroscopic data on conjugation in systems of ordinary bonds are very scarce. U. v. spectral data suggest that the intensity of Raman lines for the chains $(SiR_2)_n$, $(GeR_2)_n$, and $(SnR_2)_n$ should be strongly non-additive [93]. The intensity of the C-I line has been found [314] to be much greater in the $I-CH_2-CH_2-I$ spectrum than in the $I-(CH_2)_3-I$ spectrum.

XV. APPLICATIONS OF RAMAN LINE INTENSITY STUDIES

The previous Sections have been concerned with the application of Raman line intensity data to the study of mutual effects of atomic groups. In addition, a great deal of work has been done on the application of line intensity data to the choice of the correct structural formula for new compounds (see examples in Ref. 315), to determine

conformation, to study tautomerism, association, ionisation, and symmetry in molecules, and also to assign spectral lines to particular types of vibration (see examples in Ref. 15).

Bobovich and coworkers have established the structure of various products which could not be characterised by chemical methods [316-318]. By measuring the intensity of the lines for the benzene ring, the double bonds, and the nitro group in the products of the reaction of bromonitrostyrene with β-dicarbonyl compounds, they were able to choose the correct structure from four possible alternatives, to disprove the originally suggested structure involving conjugation of the nitro group and the phenyl group, and to establish the presence (and the type) of enolisation [318]. The positions of the double bond in phenylaminotriazole and of the acyl group in its acylation products have been established [317]. Six C_6Cl_8 compounds have been assigned to well defined isomeric forms by choosing between fourteen possible structural formula (though not always convincingly) [319].

Shorygin and Alaune [237] have determined the position of equilibrium in salt formation in "aromatic amine + organic acid" systems. Thiocyanato complexes have been examined [188], with the conclusion that mercury is attached to the ligand groups through largely covalent bonds with S atoms, zinc is attached to the same atom through weakly covalent bonds (low value of α'), whereas cadmium is attached to C atoms. The spectra of nitrates in aqueous solution have been studied, and it has been shown that ion pairs ($Zn^{2+} + NO_3^-$) are formed in which the anion has a lower symmetry, and that a covalent bond exists in indium nitrate [320]. From the intensity of cyanate lines it has been suggested [253] that the Au–C bond has some double bond character. Association has been investigated in acetamide [221], benzene [130], and other compounds. The angular rotation of the fragments of the biphenyl molecule has been evaluated from the intensity of the benzene lines [321]. Other applications of Raman line intensity data include the determination of the relative amounts of *s-cis* and *s-trans* isomers in liquid pentenone [322], the determination of the energy difference between the *s-cis* and the *s-trans* isomers of acrolein [323], and the interpretation of u.v. absorption bands [324].

These examples are sufficient to indicate the versatility of the method; its possibilities are far from exhausted, and there is every reason to hope that effort in this direction will be intensified.

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Infrared Absorption Spectra of Aliphatic Nitro-compounds and Their Derivatives

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Data on the infrared spectra of aliphatic nitro-compounds and their salts are discussed and summarised. Relations are established between the position of the nitro-stretching bands in the absorption spectrum and the structure of the radical. A fairly large number of examples are given of the use of infrared spectroscopic data to elucidate the detailed structure of nitro-compounds and their salts, and also to study the behaviour of these compounds in various media. Problems of the assignment of the vibrations in nitro-compounds and in the salts of mononitro- and polynitro-compounds are examined. Possible uses of the infrared relations to identify and analyse nitro-compounds and their derivatives are illustrated. The bibliography contains 237 references.

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I. INTRODUCTION

The rapid development of the chemistry of aliphatic nitro-compounds and improvements in the technique of obtaining infrared absorption spectra have led to the accumulation of much factual information on the infrared spectra of nitro-compounds. However, this information is scattered among numerous papers, and no monographs or reviews have hitherto been published on this topic. The present Review discusses and summarises existing data on the infrared spectra of aliphatic nitro-compounds and their salts, and the relations found are used to elucidate the detailed structure of nitro-compounds and to identify them.

II. ASSIGNMENT OF MAIN ABSORPTION BANDS OF NITRO-COMPOUNDS

What are probably the first papers on the infrared spectra of nitro-compounds[1-4] do not discuss the problem of assigning the absorption bands to definite vibrations. From 1940 several papers appeared[5-11] whose authors assigned bands by comparing the infrared and the Raman spectra (intensity and degree of depolarisation) of nitromethane[5-10], its derivatives[6,7,10], and its homologues[5-7,11]. During the same period stretching vibrations of nitro-groups and the carbon–nitrogen bond in certain nitroalkanes and their halogeno-derivatives were assigned by Wittek[12,13] on the basis of the Raman spectra. A later paper by Wittek[14] makes assignments also in polynitroalkanes. Assignment is a fundamental problem in the calculations and in various correlations between structure and spectral characteristics, etc. This makes it clear why papers have hitherto appeared with complete[15-26] or partial[27-33] (stretching vibrations of the nitro-group and the carbon–nitrogen bond—sometimes only stretching vibrations of the nitro-group) assignment of the bands observed in the spectra of nitro-compounds.

Analysis of the papers[19-21,26-38] shows that the antisymmetric stretching vibration ν_{as} of the nitro-group in a series of aliphatic nitro-compounds and their derivatives appears as an intense band in the range 1640–1535 cm^{-1}. Splitting of this band is observed[16,29,42] only with tetranitromethane†. Other absorption bands are usually absent from this range‡, so that the assignment of ν_{as} presents no difficulty. The symmetric stretching vibration ν_s of the nitro-group appears in the range 1385–1280 cm^{-1}, which contains other bands, and there is no generally accepted view concerning the assignment of this vibration. Thus Wittek[13], and following him Iogansen and Litovchenko[29], assign two bands in nitromethane and some of its homologues to ν_s, assuming that the appearance of two bands is due to mechanical interaction between deformation vibrations of the methyl group δCH_3 and the symmetric stretching vibration of the nitro-group. The chief argument of these authors is that the Raman spectrum contains two fairly intense and equally polarised ($\rho \simeq 0.4$) bands in the range 1410–1365 cm^{-1}. In the Reviewer's opinion the assignment of the two bands to ν_s of the nitro-group is unjustified. Such assignment involves the assumption that the intensity of the deformation vibration δCH_3 or δCH_2 is independent of the introduction of electronegative substituents. This is not observed. The introduction into a molecule of strongly electronegative groups such as nitrate[43], sulphonyl chloride[44], etc.[21] produces the same

† The splitting of ν_{as} observed in the spectrum of trinitroethanol[29] is not confirmed by other workers[39-41].

‡ Aliphatic–aromatic trinitromethyl derivatives form an exception[31].

effect as that of the nitro-group: a quite intense polarised ($\rho \simeq 0.4$) band appears in the region of 1400 cm^{-1}, although there can be no question of any mechanical interaction in the case of nitrates, sulphonyl chlorides, etc. It is not surprising, therefore, that other workers[5,6,8-10,15,19-22,27,31,32,34,35,45], including Wittek in a later paper[14], assign only one, lower-frequency band to ν_s in nitromethane and its homologues. The correctness of this assignment is confirmed by experimental data on the infrared spectra of nitromethane labelled with ^{18}O [46]: the introduction of "heavy" oxygen into nitromethane produces a shift in only one, the longer-wavelength band (from 1375 to 1357 cm^{-1}), while the band at 1396 cm^{-1} remains unchanged.

The origin of the splitting of ν_s of the nitro-group in *gem*-dinitro- and 1,1,1-trinitro-compounds is less certain. One absorption band in the infrared spectra of these compounds is usually assigned to ν_s[28,31,32,34,35,37-41,47-59]. Several authors, however, assign two bands to ν_s of the nitro-group[14,25,29,30,60], such assignment again being based on the Raman spectra. The second band in the infrared spectra§ often appears as a shoulder[25]. Furthermore, theoretical calculation has shown[60] that only a small part of the splitting (which totals 50–60 cm^{-1}) can be attributed to mechanical interaction. (Most authors[14,25,29] explain the splitting of ν_s of the nitro-group by mechanical interaction of the vibrations.) It seems to the Reviewer that Raman spectral data cannot be used unequivocally for interpreting ν_s of the nitro-group. Thus the Raman spectrum of chloropicrin contains two intense bands (1306 and 1345 cm^{-1})[12] having similar degrees of depolarisation ($\rho \simeq 0.5$). Nevertheless, in this case all authors assign only one of these bands to ν_s[12,14,17,18,26,27]. Hence the appearance of a second intense polarised band ($\rho \simeq 0.40$) in the Raman spectrum is still not an unambiguous criterion that it is due to a symmetric stretching vibration of the nitro-group.

Assignment of the remaining absorption bands to definite modes of vibration can be found in Refs. 9, 10, 18–26, and 42, but these bands are rarely used in everyday practice, and therefore will not be discussed here.

Useful information on the general form of the infrared spectra of certain nitro-compounds or on the ranges of absorption characteristic of the nitro-group can be found in Refs. 61–68.

III. CALCULATION OF MECHANICAL MODEL OF VIBRATIONS OF NITROALKANES. ELECTRO-OPTICAL PARAMETERS OF NITROMETHANE

The first calculations of the vibration modes of nitroalkanes were made independently in three papers[7-9]. Mathieu and Massignon[7] and Bogdan and Stefănescu[8] calculated for a planar tetra-atomic model of $C-NO_2$ with symmetry C_2. In both cases the frequencies obtained agree well with experiment. Wells and Wilson's[9] calculation regarded nitromethane as two non-bonded groups NO_2 and CH_3, having symmetry C_{2v}. Two years later Wilson[10] refined this calculation, having supplemented the experimental data with the spectrum of trideuteronitromethane; he assumed that neither the geometry nor the potential function of the molecule is changed when hydrogen is replaced by deuterium.

Popov and Shlyapochnikov[60,69] have recently made a fundamental calculation for nitroalkanes (nitromethane, nitroethane, 1,1-dinitroethane, and trinitromethane). They computed the frequencies and modes of the normal vibrations for the mononitroalkanes[69], and determined the sensitivities of the frequencies to variation in the force constants. They conclude[69] that vibrations of the $C-NO_2$ fragment are uncharacteristic in frequency and in mode. The most characteristic is the ν_{as} vibration of the nitro-group. This conclusion does not agree with the views of Müller and Nagarajan[70], who conclude, though from a simpler calculation of a planar tetra-atomic model of $C-NO_2$, that the methyl group has little effect on the skeletal vibrations of the $C-NO_2$ grouping.

The mechanical problem for the 1,1-dinitroethane and trinitromethane molecules has not, in the view of the authors themselves[60], been solved with sufficient accuracy. Nevertheless, their analysis leads them to the conclusion that the force field of the $C-NO_2$ group undergoes no great change on passing from nitromethane to the above molecules. Interaction of the nitro-groups in polynitroalkanes does not directly affect the elastic properties of the nitro-group, but is apparent only on adjacent CN bonds¶.

Solution of the mechanical problem for the nitromethane molecule[69] and experimental data on the absolute integrated intensities of the infrared bands of nitromethane and trideuteronitromethane vapours enabled Popov and Shlyapochnikov[71,72] to determine the electro-optical parameters of the nitro-group—the dipole moments of the bond and their derivatives with respect to the vibrational coordinates. From the results it is concluded[71,72] that the dipole moment of nitromethane is determined in considerable measure by that of the carbon–nitrogen bond (μ_{CN} = 1.8 D). Somewhat later an analogous electro-optical problem for nitromethane was solved by Singh[73]. However, he considers that the differences between dynamic and static dipole moments are due to errors in the calculations, and that the agreement between them can be improved by taking into account the suggestions made by Sverdlov[74,75].

IV. INTENSITY OF ABSORPTION BANDS OF NITRO-COMPOUNDS

As already noted, the nitro-stretching bands are quite intense: the molar extinction coefficient ϵ (M^{-1} cm^{-1}) for the ν_{as} band in nitroalkanes is ~ 500 [28,29,76-79] per nitro-group, whereas ϵ for ν_s of the nitro-group is ~ 100 [28,29,78]. The appearance of conjugation is accompanied by some decrease in $\epsilon\nu_{as}$, whereas $\epsilon\nu_s$ increases[28,29,80]. Data on the integrated intensities† of the nitro-stretching vibrations (ν_{as} and/or ν_s) will be found in Refs. 29, 56, 60, 73, 80, 83–86‡. The integrated intensity A_{as} of the antisymmetric vibration of the nitro-group is found to be additive[29,60,91], varying little with the structure of the radical.

§ Unfortunately the type of spectrum (infrared or Raman) is not indicated in Ref. 30, nor the intensity and degree of depolarisation of the bands.

¶ The invariability of the elastic properties of the nitro-group is not confirmed (see below) by the dependence of ν_{as} for the nitro-group on the inductive effect of the substituent[31].

† For the theory of integrated intensities, their experimental determination, and conversion coefficients between various intensity scales see, for example, the reviews[81,82].

‡ Data on the integral intensities of the nitro-stretching vibrations in nitro-aromatic compounds will also be found in Refs. 87–90.

On the other hand, the intensity A_S of the symmetric vibration depends substantially on the structure of the radical[29,80,83,86,91], and several workers have suggested[83,86,91] that A_S should be used as a measure of conjugation between the nitro-group and the rest of the molecule in conjugated and aromatic nitro-compounds.

Intensities of other bands have been measured only for nitromethane (at ~ 1105[92], 915[73,92], and 656[73] cm^{-1}). The temperature variation in the intensities of two bands (1103 and 917 cm^{-1}) of nitromethane has also been investigated[92].

V. EFFECT OF STATE OF AGGREGATION AND SOLVENT ON INTENSITY AND POSITION OF ABSORPTION BANDS OF NITRO-COMPOUNDS. HYDROGEN BONDS

The effect of the solvent on the position of the nitro-stretching bands has been examined in only four papers[78,84,93,94]. All the authors conclude that solvents produce only slight shifts in the frequencies of both bands§. More detailed examination of the effect of the solvent on the position of the absorption bands indicates a fairly substantial effect on ν_{as} with change in the state of aggregation (transition from the gaseous state to the liquid) and on passing from the gaseous state to solutions, but this effect reduces to zero as nitro-groups accumulate on the same carbon atom. Nevertheless, the values of ν_{as} and ν_S of the nitro-group are almost unaffected in "inactive"¶ solvents[31]. Values of ν_S diminish somewhat on passing from liquid mononitro-compounds to their solutions. Table 1 gives examples illustrating the influence of the solvent on the frequencies of the nitro-group.

The integral intensity of the absorption bands due to the nitro-group also is almost unaffected by the solvent[79,84]. It is interesting that, in contrast to the frequencies, the intensity of the antisymmetric nitro-stretching vibration A_{as} in nitromethane is the same, within the limits of experimental accuracy, in the gas and in solution: $A_{as,soln}/A_{as,gas} = 1.04 \pm 0.06$.[85]

Study of the intramolecular† and the intermolecular hydrogen bonding of nitro-alcohols and nitro-amines, and also of intermolecular hydrogen bonding between various proton-donors and nitro-compounds, is very closely linked with questions of the effect of the solvent on the vibration frequencies of nitro-compounds.

Urbanski[97-100] assumed that nitro-alcohols and nitro-amines form six-membered rings by interaction of the nitro-group with the hydroxyl or the amino-group. He considered that this hypothesis was supported by the displacement of the nitro-stretching vibrations to lower frequencies on the introduction of hydroxymethyl or an amino-group. This effect was intensified by the introduction of two or three hydroxy-groups. Later investigators have assumed that such an effect[31,36,39,40,78,84], if it exists at all, is usually‡ too small to be determined from the positions of ν_{as} and ν_S for the nitro-group. In the application of infrared spectroscopy to the study of hydrogen bonds in a series of nitro-compounds, therefore, the variation in the position, form, intensity, and half-width of the absorption band due to A–H stretching vibrations was determined (AH being a proton-donor compound)[39,40,78,102-108]. The investigations show that the nitro-group is a weak acceptor of hydrogen atoms[40,78,102,103,105,107].

Table 1. Position of nitro-stretching bands for nitromethane and its derivatives in different states of aggregation and solvents.

Compound	Solvent (state)	Frequencies, cm^{-1}			
		ν_{as}	$\nu_{as} - \nu_{as,av}$	ν_S	$\nu_S - \nu_{S,av}$
CH_3NO_2 [a]	gas	1582 [9,60]	19	1384 [9,60]	11
	gas	1586 [15]	23	1377 [15]	4
	liquid	1567 [34]	4	1379 [34]	6
	liquid	1563 [93]	0	1376 [93]	3
	n-butylamine	1548 [93]	−15	[b]	—
$CH_3CH(NO_2)_2$ [d]	gas	1593 [60]	12	1343 [60 c]	10
	liquid	1582 [52]	1	1331 [52]	−2
	CCl_4	1581 [29]	—	1333 [29 c]	—
$HC(NO_2)_3$ [d]	gas	1600 [60]	−8	1305 [60 c]	6
	liquid	1597 [34]	−11	1307 [34]	8
	CCl_4	1608 [40]	—	1299 [40]	—
$C(NO_2)_4$ [e]	gas	1648 [42] / 1618 [e]	6 / 5	1278 [42]	11
	liquid	1648 [42] / 1618 [e]	6 / 5	1272 [42]	5
	$CHCl_3$	1642 [29] / 1613 [e]	— / —	1267 [29]	—

(a) The frequencies $\nu_{as,av}$ and $\nu_{S,av}$ have been taken as 1563 and 1373 cm^{-1} respectively, the mean values for a solution of nitromethane in carbon tetrachloride[46,78,84,93].

(b) Region of strong absorption by the solvent.

(c) The authors assume that ν_S is split, and they give values for two bands (see above). Only the longer-wavelength component has been taken here.

(d) The means $\nu_{as,av}$ and $\nu_{S,av}$ have been taken to be the corresponding values of ν_{as} and ν_S for the compounds in carbon-tetrachloride solution.

(e) The means $\nu_{as,av}$ and $\nu_{S,av}$ have been taken to be the corresponding values for a solution of tetranitromethane in chloroform.

On the basis of infrared data Flett assumed[104] that 2-nitroethanol contained only intermolecular hydrogen bonds, whereas Krueger and Mettee consider[103] that an intramolecular hydrogen bond is formed between hydroxy- and nitro-groups in 2-nitro-alcohols, which stabilises the gauche form relative to the *trans*-form.

§ Small shifts in the frequencies of the nitro-group under the influence both of different solvents and of the state of aggregation are maintained also in a series of aromatic nitro-compounds[95].

¶ "Inactive" solvents are those which do not form complexes with the compounds under investigation.

† Tichy[96] has reviewed the use of infrared spectroscopy to detect an intramolecular hydrogen bond in organic compounds. However, he pays little attention to the formation of hydrogen bonds in nitro-compounds.

‡ Exceptions can be found in two papers. Ungnade et al.[93] found a shift of 15 cm^{-1} for ν_{as} of the nitro-group in n-butylamine solutions. This effect became considerably weaker on passing to solutions of nitromethane in n-hexylamine, and was completely absent in its solutions in secondary or tertiary alkylamines. The authors of the second paper[101] observed that the position of ν_{as} for the nitro-group remained unchanged on passing from nitro-amines to their hydrochlorides, while the ν_S frequencies changed. This displacement was attributed to formation of an intramolecular hydrogen bond.

Kuhn and his coworkers found[108] that 2-nitroethanol exists both in a *trans*-form and in a gauche form in the gaseous state and in carbon-tetrachloride solution. In the liquid state it is associated by intermolecular hydrogen bonding. It is true, of course, that many assignments in these papers[103,108] are based not on fact but on hypothesis. Urbanski's observation[97-100] of a variation in nitro-stretching frequency is due, in the Reviewer's opinion, to inductive and steric[31] effects (see Section VI). Quantitative results are listed in Table 2.

Table 2. Effect of β-hydroxy-groups on nitro-stretching bands in aliphatic nitro-compounds.

Compound[a]	Solvent (state)	ν_{as}, cm^{-1}	σ*[b]	Eqn.[c]	ν_{calc}, cm^{-1}	$\nu_{as}-\nu_{calc}$, cm^{-1}	ν_s, cm^{-1}	$\nu_s-\nu_s$ nitro-alkane, cm^{-1}[d]
$CH_3CH_2NO_2$	$CHCl_3$	1554 [29]	−0.100	(I)	1550	4	1366 [29]	—
$HOCH_2CH_2NO_2$	liquid	1555 [28]	0.20	(I)	1555	0	1370 [28]	−4
$CH_3CHClNO_2$	liquid	1571 [24]	0.95	(II)	1565	6	1355 [24]	—
$HOCH_2CHClNO_2$	liquid	1571 [36]	1.25	(II)	1570	1	1353 [36]	−2
$CH_3CHBrNO_2$	liquid	1567 [24]	0.90	(II)	1564	3	1354 [24]	—
$HOCH_2CHBrNO_2$	liquid	1566 [36]	1.20	(II)	1569	−3	1353 [36]	−1
$CH_3CH(NO_2)CH_3$	liquid	1553 [45]	−0.19	(II)	1547	−6	1357 [45]	—
$HOCH_2CH(NO_2)CH_2OH$	CH_2Cl_2	1560 [40]	0.40	(II)	1556	4	1361 [40]	4
$(CH_3)_3CNO_2$	liquid	1538 [45]	−0.30	(III)	1535	3	1344 [45]	—
$CH_3C(NO_2)(CH_2OH)_2$	CH_2Cl_2	1543 [40]	0.30	(III)	1547	−4	1347 [40]	3
$(HOCH_2)_3CNO_2$	paraffin oil	1555 [39]	0.60	(III)	1553	2	e	—
$(HOCH_2C(NO_2)(C_2H_5)CH_2)_2-\overset{+}{N}H_2Cl^-$	paraffin oil	1563 [100]	0.89	(III)	1559	4	1342 [100]	2
$CH_3C(NO_2)_2CH_3$	liquid	1575 [34]	1.53	(V)	1572	3	1330 [34]	—
$HOCH_2C(NO_2)_2CH_3$	CH_2Cl_2	1577 [39]	1.83	(V)	1576	1	1326 [39]	−4
$HOCH_2C(NO_2)_2CH_2OH$	CH_2Cl_2	1580 [40]	2.13	(V)	1581	−1	1328 [40]	−2

(a) Nitroalkanes given for comparison.

(b) Necessary values of σ* taken mainly from Ref. 109. Value of σ* for the nitro-group taken from Ref. 110; and $\sigma^*_{RNH_2CH_2^+}$ calculated from values of σ_I.[111]

(c) For equations used in calculation see Table 3.

(d) This column gives the difference between ν_s for the given nitro-alcohol and ν_s for the corresponding nitroalkane.

(e) Values of ν_s not given here, since the papers show a significant lack of consistency in their values[97,98].

This conclusion is supported also by the fact that the absorption band ν_{as} of the nitro-group in nitromethane is almost identical in methanol and in carbon tetrachloride[78], although the latter is an "inactive" solvent, whereas nitromethane forms intermolecular hydrogen bonds with methanol. In other words, the ν_{as} frequency of the nitro-group remains unchanged independent of the presence or the absence of hydrogen bonds, provided that the inductive and steric effects of the nitro-compound remain constant.

β-Nitro-alcohols are capable of partial association in solvents such as carbon tetrachloride[105] or of the formation of stable intermolecular complexes with pyridine[39,106]. In all cases the association constants of the complexes increase with increase in the number of β-nitro-groups[39,105,106].

In concluding this Section we may note several investigations in which nitromethane has been used as solvent, the second component (the proton donor) being water[112-114], phenol[115,116], or a derivative of the latter[116]. Nitromethane has been investigated as solvent also in study of the integral intensity A_{CN} of the C≡N stretching band in benzonitriles and the dependence of A_{CN} on the Hammett σ-constant[117], and also in study of the dependence of the integrated intensity and the half-width of the chloroform band at ~ 760 cm^{-1} on the nature of the solvent[118].

VI. RELATION BETWEEN POSITION OF BANDS DUE TO NITRO-STRETCHING VIBRATIONS AND STRUCTURE OF THE NITRO-COMPOUNDS

A relation between the positions of symmetric and antisymmetric nitro-stretching bands has been sought by several workers. Some have observed[28,95,119,120] a linear relation between ν_{as} and ν_s, although two kinds of straight lines—for electronegative and for electropositive substituents—are present with aromatic nitro-compounds[28,95,120]. Only Flett[90] observes that such a relation does not exist. Iogansen and Litovchenko[91] consider that "the stretching frequencies of the nitro-group correlate poorly with the structure of the molecular residue if they are examined separately and all nitro-compounds are covered". These workers therefore propose to correlate

$$\nu_{av} = \frac{\nu_{as}+\nu_s}{2} \text{ with } \Delta\nu = \nu_{as} - \nu_s.$$

This is regarded[91] as dividing the nitro-compounds into classes, although there is no relation at all between ν_{av} and $\Delta\nu$ (these quantities are discussed below).

Attempts have also been made to find a correlation between ν_{as} of the nitro-group and the effective electronegativity χ of the α-carbon atom[35,121]. A linear relation was demonstrated between these parameters.

Finally, several authors have sought a relation between ν_{as} for the nitro-group and the Hammett and Taft σ-constants[28,31,72,119,120,122-126]. Campbell and Gilow[127] made a theoretical examination of the relation between the σ-values and the shift $\Delta\nu$ in the absorption bands, and discovered the relation

$$\Delta\nu \frac{hC}{2.3\,RT} = -\rho\cdot\sigma - \frac{\Delta(\Delta S)}{2.3\,R} \qquad (1)$$

where h is Planck's constant, C the velocity of light, R the gas constant, T the absolute temperature, ρ a constant, σ the inductive constant of the substituent, and $\Delta(\Delta S)$ a measure of the change in entropy. From this formula a linear relation is to be expected between σ and the shift (in cm^{-1}) in the absorption bands, provided that the term $\Delta(\Delta S)$ is constant. This condition is satisfied if the effect of the solvent is excluded or if it remains constant for a given reaction series. The second, not unimportant condition determines the choice of reaction series. Both conditions were observed in investigations[28,31,72,119,120,122-126] where a linear relation was found between ν_{as} and the Taft and Hammett σ-values. As example Table 3 is taken from a paper[31] in which a large number of nitro-compounds were used to find relations between ν_{as} and the σ*-values.

From the data in Table 3 and the effect of conjugation on the asymmetric nitro-stretching frequency Slovetskii[31] concludes that this frequency is influenced by the inductive and steric effects and also by conjugation. The influence of the steric effect is evident only on passing from nitro-compounds containing one or two α-hydrogen atoms to compounds which do not contain them. The role of the inductive effect has been discussed above. In the simplest cases the effect of conjugation is additive. α-Fluorine atoms exert only an inductive effect. The experimental results[17,18,128-138] do not reveal the presence of a steric or other specific effect.

Analysis of the influence of various factors on the position of the symmetric nitro-stretching frequency in a series of aliphatic nitro-compounds led Slovetskii[31] to the conclusion that the main factor is the steric effect. The shifts in the ν_S frequencies due to the steric effects of different substituents are additive, being dependent on the volume of the substituent but independent of its electron-accepting or donating properties. The inductive effect and the conjugation factor have hardly any influence on the position of ν_S for the nitro-group.

Table 3. Dependence of antisymmetric nitro-stretching frequency ν_{as} on inductive effect σ^* of substituent[31]: $\nu_{as} = \nu_0 + \rho\sigma^*$.

Reaction series[a]	ν_0, cm^{-1}	ρ	Limits		r[b]	s[c]	Quantity of cpd.
			ν_{as}, cm^{-1}	σ^*			
(I) RCH_2NO_2, where R = alkyl, substituted alkyl, or electronegative substituent	1552	16	1578 1546	1.05 −0.15	0.77	4.5	77
(II) $R'R''CHNO_2$, where R', R'' = alkyl, substituted alkyl, electronegative substituent (other than NO_2), or any combination thereof	1550	16	1590 1548	2.15 −0.26	0.85	6.9	74
(III) $R'R''R'''CNO_2$, where R', R'', R''' = alkyl, substituted alkyl, electronegative substituent (other than NO_2), or any combination thereof	1541	20	1610 1534	3.15 −0.37	0.96	6.2	42
(IV) $RCH(NO_2)_2$, where R = alkyl, substituted alkyl, or any electronegative group	1556	13	1608 1570	3.46 1.60	0.85	4.5	24
(V) $R'R''C(NO_2)_2$, where R', R'' = alkyl, substituted alkyl, any electronegative group, or combination thereof	1547	16	1630 1572	5.19 1.53	0.96	3.9	42

(a) All kinds of nitro-compounds, containing any α-substituent other than fluorine, have been used. α-Fluoro-nitro-compounds fall into the reaction series in which a hydrogen atom(s) is present instead of the fluorine atom(s)[31].

(b) r = correlation coefficient.

(c) s = standard deviation.

Thus the positions of the nitro-stretching bands (ν_{as} and ν_S) depend to different extents on steric, inductive, and conjugation effects. Hence the quantities $\Delta\nu = \nu_{as} - \nu_S$[34,91] and $\nu_{av} = \frac{1}{2}(\nu_{as} + \nu_S)$ are fairly random quantities, and it is not surprising, therefore, that no relation was found[91] between them. Contradictory views are held concerning the relation between ν_{as} and ν_S.[28,90,95,119,120]

VII. ABSORPTION BANDS DUE TO ANIONS OF MONO- AND POLY-NITRO-COMPOUNDS§

1. Anions of Mononitro-compounds

The infrared spectrum of the sodium salt of 1-nitropropane was first determined by Mathieu and Massignon[5].

§ We apply the term polynitro-compounds to compounds having at least two nitro-groups attached to the same carbon atom.

Comparison of the infrared and Raman spectra of these compounds enabled the strong band at 1586 cm^{-1} to be assigned to the C=N bond. These workers also noted that the characteristic frequencies of the nitro-group and also of the carbon–nitrogen single bond disappear on passing from 1-nitropropane to its sodium derivative.

A complete assignment of the infrared absorption bands due to salts of nitromethane[139-141] and 2-nitropropane[139] has been made much more recently. Jonathan[139] concludes from the spectral data that the anions have a planar structure with the carbon–nitrogen bond order close to 2: $[CH_2{=}NO_2]^-Na^+$ and $[(CH_3)_2C{=}NO_2]^-Na^+$. Such a structure is supported by all the spectral data and by molecular-orbital calculation. Brookes and Jonathan[140] used the sodium salt of trideuteronitromethane and improved the assignments of ν_S of NO_2^- (the charged nitro-group) in the infrared spectrum of the sodium derivative of nitromethane. Yarwood and Orville-Thomas[141] consider, contrary to the opinion of Jonathan and Brookes[139,140], that the carbon–nitrogen bond in this sodium derivative is close to a single bond and that the anion has a non-planar structure. The authors[141] arrive at this view—erroneous¶ in the Reviewer's opinion—as a consequence of the unsubstantiated statement that the position of carbon–hydrogen stretching vibrations depends solely on the type of hybridisation. All the other investigators[143-148] have found, in the infrared spectra of salts of mononitro-compounds, bands corresponding to a C=N double bond. Moreover, Buczkowski and Urbanski[144] even found two bands (~ 1660 and 1600 cm^{-1}) corresponding to C=N stretching vibrations in the salts of primary nitroalkanes, on which they based the hypothesis that the salts are able to exist in two isomeric *cis*- and *trans*-forms. However, this view is not consistent with the experimental results† (the positions of the absorption bands due to a C=N bond differ by ~ 15 cm^{-1},[149] not by 60 cm^{-1}, in *cis–trans* isomers). Furthermore, account must be taken of the hygroscopic nature of the salts of mononitro-compounds‡ and of the possible appearance of a band at ~ 1660 cm^{-1} due to bound or absorbed water[150].

The conditions of preparation of specimens for determining their infrared spectra were not specified in Ref. 144. Feuer et al.[145] made assignments of stretching vibrations of the charged nitro-group NO_2^- in the salts of nitroalkanes, α-nitro-ketones, and α-nitro-nitriles, and Kerber and Chick[147] in a nitrocyclopentadiene salt. Table 4 gives assignments in salts of mononitro-compounds made by various workers.

2. Anions of Polynitro-compounds

Brown[28] assigned two absorption bands in the infrared spectrum of the potassium salt of dinitroethane to stretching vibrations of the charged dinitromethyl group

¶ The planar structure of the nitromethane anion and the presence of a C=N double bond (the presence of vinyl hydrogen atoms) is supported by the results of another independent method—nuclear magnetic resonance spectroscopy[142].

† The *cis–trans* isomerism of salts of mononitroalkanes in solution is not confirmed by n.m.r. spectroscopy[142].

‡ Jonathan[139] emphasises that the salts which he studied were hygroscopic, and therefore the infrared spectra of the sodium salt of nitromethane varies substantially between specimens prepared with and without the use of a drying chamber.

(ν_{as} = 1242 and ν_s = 1151 cm^{-1}). Later investigators[37,49,53,151-153] note that, on passing from polynitro-compounds to their salts, bands characteristic of nitro-stretching vibrations (see above) disappear from the infrared spectra, while several new bands appear at ~ 1480, ~ 1200, and 1120 cm^{-1}. The appearance of these bands is attributed to vibrations of the dinitromethyl anion[37,49,53,151-153] and of the anion of trinitromethane[151-153], but no assignments are given. Kaplan[154] made empirical assignments for salts of polynitro-compounds by analogy with the covalent nitro-group. He assigned the band at 1269 ± 9 cm^{-1} to antisymmetric N–O stretching vibrations, and that at 1173 ± 10 cm^{-1} to the symmetric vibrations. Kamlet et al.[155] and Lippincott et al.[156] made more justified assignments of bands to vibrations of the dinitromethyl anion using the spectrum of potassium deuterodinitromethane. The latter authors[156] also adduce data on the Raman spectra of the dinitromethane anion and its deuterated analogue. Comparison of the assignments[28,154-159] shows that they do not completely coincide. A somewhat special position in this series is occupied by the work of Singh[157], whose assignments differ from those proposed by other workers[155,156] for the spectrum of potassium dinitromethane.

Slovetskii et al.[158] conclude from infrared band intensity data that the above bands are due to di- and tri-nitromethyl groups, and can be classed as group absorption bands of the corresponding anions. However, the results available at present do not enable a complete assignment to be made in the vibrational spectra of anions of polynitro-compounds. It has been concluded[159] on the basis of calculation that almost all frequencies of polynitro-carbanions are non-characteristic, 2–5 angles and bonds being involved in each vibration. Yet the calculation[159] involved force constants and in some cases bond lengths and angles of the unionised nitroalkanes, which evidently diminishes the reliability of the results. The suggested[158] specific character of the group bands due to the anions of *gem*-dinitro-compounds and trinitromethane is supported by published data[37,154,159,160]: even the presence of conjugation has hardly any effect on the position of these bands§.

Studies have been made of the effect of the solvent on the infrared spectra of the anions of *gem*-dinitroalkanes and trinitromethane[162-164]¶. Integrated and peak intensities have been measured, and determinations also made of the half-width and the exact position of the group absorption bands due to the trinitromethyl, dinitromethyl, and *gem*-dinitroethyl anions both in the crystalline state (compressed with potassium bromide) and in protic and aprotic solvents.

The investigation showed that, for a given anion, the solvent, the possible formation of ion pairs, and the nature of the cation do not influence the integrated intensity or the shape of the bands. Nor does the nature of the cation affect the position of the bands in solutions. However, change in the state of aggregation—transition from the crystalline salt to its solutions—and in the solvent affects the position of the group absorption bands, this effect being different with different bands. The character of the frequency shift as a function of the nature of the solvent led to the conclusion[162,163] that this shift was due to specific solvation of the polynitro-carbanions.

Briefly summarising available data, we can say that, in the salts of mononitro-compounds, the presence of a C=N bond has been shown fairly convincingly, and reliable assignments have been made of the frequencies due to the CNO_2^- grouping. In the salts of polynitro-compounds, however, only the group frequencies have been reliably assigned. The assignments in anions even of the same polynitro-compounds are contradictory, and require further investigation.

Table 4. Assignments of $C{=}NO_2^-$ stretching vibrations (cm^{-1}) in salts of mononitro-compounds.

Sodium salt of	Solvent (state)	C=N bond	N–O in NO_2^- as	N–O in NO_2^- s	Ref.
1-Nitropropane	paraffin oil	1586 1650 1599 1600	a a 1289	a a 1170	5 144 145
Nitromethane	emulsion in CCl_4	1618	1277 1261	1031 1016	139
	paraffin oil	1582	1272 1261	983	140
	paraffin oil	b	1580	1278 1263	141
		1587	1272	1174	145
Trideuteronitromethane	paraffin oil	1553	1233 1217	899	
2-Nitropropane	ethanol	1604	a	a	143
	paraffin oil	1608	1176 1166	944	139
		1605	1295	1168	145
Primary mononitro-alkanes	paraffin oil	1665—1635 1609—1589 1603—1587	a 1316—1272	a 1175—1555	144 145
Mononitro-compounds (K salts)	paraffin oil	a 1663—1592	1253—1205 a	1156—1124 a	145 146
Nitrocyclopentadiene	paraffin oil	1548	1368	1192 1175	147
α-Nitromethylbenzyl alcohol	paraffin oil	1560	c	c	148

(a) No assignments are given for these vibrations.

(b) The authors deny the presence of a double bond in the salt.

(c) The paper gives several absorption bands—at 1330, 1270, 1139, 1117, 988, and 955 cm^{-1}—which the authors attribute to antisymmetric and symmetric stretching vibrations of the NO_2^- group.

VIII. USE OF INFRARED-SPECTROSCOPIC METHODS TO ESTABLISH THE STRUCTURE OF ORGANIC NITRO-COMPOUNDS

1. Analytical Application

Consideration of the infrared spectra of nitro-compounds and their salts indicates that the main differences in the spectra which are suitable for analytical purposes occur in the region of nitro-stretching vibrations and group absorption bands due to nitro-carbanions. These differences consist in a certain regularity in the position and intensity of the bands depending on the structure of the compounds.

§ Conjugation in potassium bromodinitromethane is confirmed by X-ray examination[161].

¶ Shokhor et al.[164] do not give experimental data, but merely mention that the infrared spectra of solutions of the alkali-metal salts of trinitromethane exhibit a close similarity independently of the cation and the solvent.

Thus primary and secondary nitroalkanes can be distinguished from tertiary nitroalkanes by the bands due to antisymmetric and symmetric stretching vibrations of the nitro-group, and primary from secondary compounds by the symmetric nitro-stretching band[28,34,45].

A detailed examination of published data[165-189] supports this conclusion, with substances belonging to this group which have functional substituents quite remote from the nitro-group (in any case so long as the inductive effect does not operate[31]). The accumulation of nitro-groups on the same carbon atom leads to shifts in the antisymmetric and symmetric vibrations of the nitro-group to higher and lower frequencies respectively[34], which can also be utilised for analytical purposes[27,28,34,59,182,183,190-194]. Another extremely interesting fact is that the difference in frequency between antisymmetric and symmetric nitro-stretching vibrations ($\Delta\nu = \nu_{as} - \nu_s$) is also characteristic[34,91], having approximate values of 180, 250, and 300 cm^{-1} for mononitroalkanes, *gem*-dinitroalkanes, and 1,1,1-trinitroalkanes respectively. Hence this difference also can be used to distinguish among mono-, di-, and trinitro-compounds. However, the difference ceases to be characteristic when we pass to nitro-compounds having a halogen atom or other functional group in the α-position. In this case considerably greater assistance for analytical purposes may be obtained from the dependence of the position of the stretching bands on the structure of the nitro-compounds (see Section VI), in particular the relation between ν_{as} and the σ^*-values[31]. Table 5 gives as examples a few calculations of ν_{as} (based on the equations in Table 3) and of ν_s. For further details see Slovetskii's paper[31].

Table 5. Calculation of positions of ν_{as} and ν_s bands of nitro-group[a].

Compound	State solvent	ν_{as}, cm^{-1}	σ^*[b]	Eqn. (Table 3)	ν_{as}, calc', cm^{-1}	$\nu_{as} - \nu_{as}$ calc', cm^{-1}	ν_s, cm^{-1}	ν_s, calc', cm^{-1}
$CH_2FCH_2NO_2$	liq.?	1557 [195]	0.40	(I)	1558	−1	1370 [195]	1370
$(C_6H_5)_3CCH(NO_2)COOC_2H_5$	CCl_4	1565 [196]	1.04	(II)	1567	−2	1356 [196]	1359
$(CH_3)_2C(NO_2)CH_2ONO_2$	liq.	1550 [197]	0.28	(III)	1547	3	1349 [197]	1346
$CH_3C(NO_2)(CH_2ONO_2)_2$	liq.	1563 [198]	0.86	(III)	1558	5	1350 [198]	1346
$(C_2H_5O_2C)_2C(NO_2)CH_2OH$	liq.	1572 [199]	1.82	(III)	1577	−5	—	—
$H(NO_2)_3CCOOC_2H_5$	liq.?	1588 [200]	2.54	(IV)	1589	−1	—	—
$NC(NO_2)_2CCOOC_2H_5$	liq.?	1610 [200]	3.84	(V)	1608	2	—	—

(a) Experimental data on the positions of the nitro-stretching vibrations can be found in Refs. 201–218 and also in the papers cited earlier.

(b) Values of σ^* taken from Palm's paper[109], and those of σ^* for nitro and nitrate groups from Slovetskii and Fainzil'berg's paper[110]. Several of the σ^*-values can be calculated from those given for σ_I in Charton's paper[111].

A second extremely important fact for the identification of nitro-compounds is the small effect of structure on the integrated intensity of the antisymmetric nitro-stretching vibration[79,91]. This observation can be exploited to determine the number of nitro-groups in compounds of unknown structure[91].

Sometimes there is no need to measure the integrated intensity of a band, a comparison of relative intensities being sufficient, e.g. of ν_{as} and ν_s for the nitro-group[91] or of ν_{as} for two different groups[183]. On the other hand, the intensity of the ν_s band of the nitro-group is considerably dependent on conjugation[29,83,91], another fact which is useful for establishing the structure of nitro-compounds. Furthermore, infrared spectroscopy can be recommended for determining the quantitative composition of mixtures of nitromethane with its simple homologues and analogues—nitroethane, 1-nitropropane, and 2-nitropropane[219].

The transition from nitro-compounds to their anions is accompanied by disappearance of the bands characteristic of the nitro-group and the appearance of a series of bands due to the anions (see Section VII). It must be stressed that the spectrum of polynitro-carbanions is quite characteristic both in its general form and in intensity[162]. The integrated intensities of the strongest bands reach (5–6) × 10^4 cm^{-2} M^{-1} [162] (practical system of units[81,82]). In other words, the presence of an anion can be identified quite reliably from the presence of group absorption bands and measurements of their intensity.

In conclusion we note that, whether in the free form or as the anion, the dinitromethyl group has the same spectral characteristics in the aromatic and heterocyclic series as in the aliphatic series.

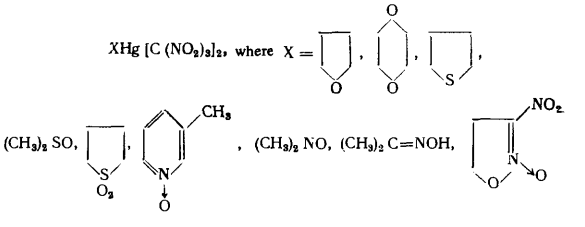
We shall discuss below some examples of the application of infrared spectroscopy to establishing the structure of and elucidating the chemical changes undergone by nitro-compounds and their salts.

2. Structure of Mercury "Salts" of Trinitromethane and Fluorodinitromethane

Infrared spectroscopy has been used to study the structure of the so called mercury salts of trinitromethane and fluorodinitromethane[163,220]. The results confirm that in the crystalline state both "salts" are true organometallic compounds: the spectrum contains bands at 1598, 1312, and 798 cm^{-1} [163,220] corresponding to the trinitromethyl group, and at 1580, 1315, and 835 cm^{-1} [163] corresponding to the fluorodinitromethyl group, while bands characteristic of the corresponding polynitro-carbanion or the covalent aci-form are absent. Bands corresponding to the trinitromethyl anion appear in the infrared spectra of aqueous and dimethylformamide solutions of bistrinitromethylmercury; the proportion of the ionised form diminishes with increase in the concentration of the compound, and may become almost zero on addition of a sufficient amount of the cation involved—Hg^{2+} (as mercuric nitrate)[163]. From these results it is concluded[163,220] that in the crystalline state the so called mercury salts of trinitromethane and fluorodinitromethane are true organometallic compounds, which are capable, under the influence of ionising solvents (protic and aprotic), of dissociating directly into ions without formation of an aci-form.

3. Complexing Power of Bistrinitromethylmercury

Chemical means have been used to isolate the complexes



Study of their infrared spectra showed the presence of frequencies characteristic of the trinitromethyl group—1600 ± 5, 1300 ± 5, and 800 cm^{-1}. [221]

4. Structure of Silver Salts of Polynitroalkanes

Infrared spectroscopy has been used to study the structure of the silver salts of trinitromethane[164,222], dinitroacetonitrile[222,223], dinitromethane[222], and 1,2-dinitroethane[222]. Comparison with the infrared spectra of the mercury and alkali-metal salts of the corresponding polynitro-compounds in the crystalline state have revealed the ionic structure of the silver salts, which are analogues of the alkali-metal salts and differ from the mercury derivatives, which are true organometallic compounds.

In solutions a quite different situation is found. In aqueous solutions of silver salts of polynitro-compounds Slovetskii and his coworkers[222,223] found that equilibrium was established between the true organometallic compound and the ionic form of the salt. The same conclusion was reached[222,223] from the appearance of bands (in the ranges 1610–1580 and 1330–1300 cm^{-1}) due to covalent tri- and di-nitromethyl groups on the addition of the corresponding cation Ag^+ (as silver perchlorate) to the solution or in the spectra of concentrated solutions (e.g. 20 M [sic] aqueous silver trinitromethane). From the infrared spectra it would seem that no other intermediate forms, such as an aci-form, are involved.

Shokhor et al.[164] studied the silver salt of trinitromethane in water and in various non-aqueous solvents. They found that in water the salt has an ionic structure. As the dielectric constant of the solvent decreases, however, the configuration of the trinitromethyl anion changes, and in benzene and dioxan solutions a band due to the covalent silver salt appears (at 1615 cm^{-1}). The appearance of a covalent form is consistent with the experimental data[222], but the change in configuration of the anion contradicts them. Thus the presence of equilibrium between ionic salt and organometallic compound[222] leads to a similar effect observed by Shokhor et al.[164]—diminution in intensity of the band at 1490 cm^{-1} and increased intensity of that at ~ 1600 cm^{-1}—while the dielectric constant of the solution does not decrease in this work[222]. It is not altogether clear why Shokhor et al.[164] find a displacement of the band in the range 1540–1560 cm^{-1}. This may perhaps be due to strong absorption by the solvent in this range. Unfortunately, these workers[164] give no data on cuvette thicknesses, and it is therefore difficult to assess the correctness of their results.

5. Structure of Salts of Polynitro-compounds with Organic Cations. Inner Salts

Infrared spectral data have been used several times[37,224-228] to assess the structure of salts formed by polynitro-compounds with organic cations.

Slovetskii et al.[224] investigated the salts formed by trinitromethane with 4-amino-1,2,4-triazole bases. The infrared spectra showed that in the crystalline state the salts had an ionic structure, the trinitromethane being present as an anion. This is confirmed by the presence of bands characteristic of the trinitromethyl anion (approximately at 1520, 1280, and 1180 cm^{-1}) and by the absence of bands characteristic of nitro-stretching vibrations in the trinitromethyl group (~ 1600 and ~ 1300 cm^{-1}). It was then concluded from the infrared spectra of the salts that the mobile [hydrogen] atom of trinitromethane reacts with two molecules of 4-amino-1,2,4-triazoles to form the so called "ionogenic structures"†. Examination of the region of amino-stretching vibrations showed that the transition from the free 4-amino-1,2,4-triazoles to their trinitromethyl salts was accompanied by displacement of the N–H stretching vibrations to higher frequencies, whereas protonation of the amino-group would have led to lower frequencies. In other words, this fact supports the view that the amino-group is not involved in salt formation. This is further confirmation, in the opinion of the authors[224], that the proton interacts only with the triazole ring in the crystalline salts of 4-amino-1,2,4-triazole.

From an infrared study Glowiak[225] concluded that the benzenediazonium "salt" of trinitromethane had an ionic structure. In the Reviewer's opinion this conclusion does not follow from the data given by this author[225]. In fact, Glowiak observed bands at 1629, 1374, and 1294 cm^{-1}, close to the bands—at 1623, 1372, and 1294 cm^{-1}—in chlorotrinitromethane and differing considerably from those—at 1529, 1418, 1302, and 1263 cm^{-1}—in the potassium salt of trinitromethane. His line of argument is that the chlorine atom in chlorotrinitromethane is appreciably positive in character, whereas the trinitromethyl group is negative. He regards the situation as similar in trinitromethylbenzenediazonium. One can agree with Glowiak's first assertion[225], that the spectra of chlorotrinitromethane and trinitromethylbenzenediazonium are closely similar. However, the opposite conclusion follows from this: since chlorotrinitromethane is a covalent compound‡, the benzenediazonium "salt" of trinitromethane is also a covalent compound—trinitromethylazobenzene. This conclusion is confirmed by comparing the spectrum of trinitromethylbenzenediazonium with that of the potassium salt of trinitromethane, which is known to be ionic.

The structure of inner salts has been established quite reliably from the infrared spectra for 1-guanidino-2,2-dinitroethane[226] and 2-dinitromethylpyridine[37] in the crystalline state. Zeldine and Shechter[226] reached this conclusion from the absence of the 1587 cm^{-1} band characteristic of the dinitromethyl group. Slovetskii et al.[37] deduced the formation of the internal salt 2-dinitromethylpyridine from the presence of absorption bands characteristic of the dinitromethyl anion (strong 1500, very strong and broad 1235, and strong 1130 cm^{-1}) and the absence of bands at 3000 and at 1575 and 1330 cm^{-1} characteristic of stretching vibrations of C–H and N–O respectively in the dinitromethyl group.

6. Structure of Dinitroacetonitrile Tetrahydrate and its Derivatives

Slovetskii et al.[72,223] used infrared spectroscopy to confirm the structure of dinitroacetonitrile tetrahydrate. This investigation was of fundamental value for the problem of tautomerism in polynitro-compounds.

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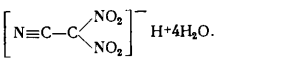
† Until the publication of Ref. 224 the formation of an "ionogenic structure" had been observed by Otting[227] only with 1,2,4-triazoles in which the 4-position was unsubstituted.

‡ That chlorotrinitromethane is a covalent compound is confirmed by various kinds of data, e.g. infrared spectroscopy[35], dipole moments[228], etc. Moreover, measurements indicate[228] that the dipole moment of the C–Cl bond is 0.23 D with the negative end of the dipole on the chlorine atom.

The infrared spectrum of the tetrahydrate proved to be identical with those of the sodium and silver salts but different from that of the *O*-methyl ether. This ether was utilised[72,223] as a fixed model compound having the same structural units—the nitro-group in its true form, the presence of a C=N bond, and the absence of a nitro-group in a charged state—as should have been present in a covalent aci-form. From the results obtained it was concluded that crystalline dinitroacetonitrile tetrahydrate had the ionic structure



Another possible ionic structure for the crystalline tetrahydrate—an internal salt—is inconsistent with the infrared spectral data[223].

7. Study of Structure of Salts of 1,1-Dinitroalkanes and Trinitromethane

Slovetskii and his coworkers[151,152] were the first to use infrared spectroscopy to study the structure of salts of polynitro-compounds. From the spectra of a large number of salts (potassium, sodium, ammonium, and lithium) of *gem*-dinitroalkanes and trinitromethane it was found[151,152] that bands corresponding to the C=N bond and also to the nitro-group in true nitro-compounds were absent from the spectra of the anions. This led to the conclusion[151,152] that the salts of 1,1-dinitroalkanes and trinitromethane contain no C=N bond (unlike the salts of mononitroalkanes[5,139,140,143-148]) and no uncharged nitro-groups, in contrast to the true form of nitro-compounds. Hence the conclusion is drawn[151,152] that all the nitro-groups in salts of polynitroalkanes are equivalent and are equally involved in formation of the anion. It is found furthermore[152] that replacement of the cation (potassium, sodium, ammonium) in the crystalline salts has little effect on the absorption bands of the anion, and from 1,1-dinitropropane onwards there are no changes at all in the spectra with different cations.

Subsequent work has shown that the spectral characteristics of the dinitromethyl anion are the same in salts of aromatic and heterocyclic derivatives[37] as in the aliphatic series. Hence the equivalence of the nitro-groups in anion formation is preserved in the aromatic and heterocyclic dinitromethyl derivatives. The equivalence of the nitro-groups in the anion is maintained in salts of dinitroacetonitrile[72,223] and also on passing to solvated anions[158,163], the configuration of the anions being almost unchanged in the crystalline salt and in solution. This conclusion is confirmed by Mel'nikov et al.,[229] who have compared experimental data on the infrared and Raman spectra of the salts of dinitromethyl derivatives, and consider that the configuration of the anions in solution differs little from the configuration in the crystal. Lippincott et al.[156] regard the infrared and Raman spectra of the potassium salts of dinitromethane and its deuterated analogue as indicating that the dinitromethane anion has a planar structure with equivalent nitro-groups.

Singh[157] assumes that the nitro-groups in the dinitromethane anion are not equivalent. However, he supports this structure with several rather artificial assignments, e.g. vibrations of the nitro-group at 1360 and 1125 cm^{-1} instead of ~ 1550 and 1380 cm^{-1}, the C=N frequency 1445 instead of 1650 cm^{-1} as usual, etc. The artificiality of the assignments and in several cases the errors in interpreting the spectrum§ cast doubt on the correctness of the structure ascribed to the dinitromethane anion.

A very large amount of experimental information on the infrared spectra of the salts of polynitro-compounds is given by Kamlet et al.[155] In their opinion 1,1-dinitrocarbanions need not necessarily have equivalent N–O bonds. In particular, the "cationic effect" may lead to non-equivalence of the nitro-groups and hence to broadening or splitting of the absorption bands. It must be stressed that no bands which could have been assigned to a covalent nitro-group are found in any of the spectra of the 32 salts investigated[155].

Non-equivalence of the nitro-groups owing to their rotation about the C–N bond with increase in the order of the N–O bonds and a corresponding increase in the ν_{as} and ν_{s} frequencies to values approaching those of unionised aliphatic mononitro-compounds are assumed only by Shokhor et al.[164] They base this conclusion on the appearance of a band in the range 1600–1500 cm^{-1} in the spectra of alkali-metal salts (from lithium to caesium) of trinitromethane and methyl dinitroacetate and the appearance of a shoulder in the range 1320–1310 cm^{-1} in the case of the trinitromethane salts. However, later work[158,163] has shown that the appearance of a band in the region of 1550 cm^{-1} in the spectrum of the trinitromethane anion is due to splitting of the band at ~ 1515 cm^{-1}. No other bands characteristic of the $C-NO_2$ grouping are observed in the spectra, even in the region of the symmetric nitro-stretching vibration. Incidentally, the equivalence of the nitro-groups in the anions of polynitro-compounds in solution is confirmed by ^{14}N n.m.r. results[230].

8. Some Other Cases of the Use of Infrared Spectra to establish the Structure of Nitro-compounds

By analogy with the structure of anions of *gem*-dinitro-compounds it might be expected that in polynitroimidazoles, e.g. in 4,5-dinitroimidazole, both nitro-groups would be equally involved in formation of the anion. Epishina et al.[231] established from the infrared spectra that with nitroimidazoles anion formation always occurs at one nitro-group with conversion of the imidazole into an isoimidazole ring.

Infrared spectroscopy has been used also to establish the structure of α-nitro-ketones[144,232]. Acyclic α-nitro-ketones are shown to exist in the keto-form, whereas the alicyclic compounds exhibit a tendency to enolisation (up to 30%). Shlyapochnikov et al.[233,234] concluded from the infrared and Raman spectra that in halogenated trinitromethane derivatives the NO and C–Hal bonds are conjugated.

Ivanov and his coworkers have been able to show by means of infrared spectroscopy that the product of the self-condensation of 1,1-dinitroalkanes is a nitrolic ester[56]. They have also completely confirmed the structure of the *O*-ethyl ethers of dinitromethane and trinitromethane[38].

Slovetskii et al.[34] used infrared spectral data to show the effect of one, two, and three nitro-groups on the antisymmetric stretching vibration of C–H in the methyl group. This effect can be traced as far as the fourth

§ Singh[157] did not observe the intense C–H stretching band in the dinitromethane anion[155,156], explaining this fact, and also the unusual assignment, in terms of the theory of resonance.

carbon atom in the case of mononitroalkanes, the fifth in *gem*-dinitroalkanes, and the sixth in 1,1,1-trinitroalkanes.

Einberg[235] used infrared spectral data to assess the structure of 5-dinitromethyltetrazole and its mono- and di-salts. Although the assignments of bands to vibrations of the nitro-groups in the salts can be disputed, his conclusion that the hydrogen atom in the dinitromethyl group is more mobile than the hydrogen atom of the tetrazole ring is not open to doubt.

Table 6. Frequencies characteristic of different types of nitro-compounds*.

Compound	Frequency, cm^{-1}		$\Delta\nu = \nu_{as} - \nu_s$, cm^{-1}	Ref.
$R'CH_2NO_2$	1554±6;	1382±6		34
$R'R''CHNO_2$	1550.5±2.5	1360.5±3.5	180	34
$R'R''R'''CNO_2$	1538.5±4.5	1348.5±4.5		34
$R'HC(NO_2)_2$	1578.5±3.5	1329±2	~250	34
$RC(NO_2)_3$	1600±3	1302.5±4.5	~300	145
$[R'RC(NO_2)]^-M^+$	1253—1205	1156—1124	—	152
$[RC(NO_2)_2]^-M^+$	~1480, ~1210, ~1120		—	152
$[C(NO_2)_3]^-M^+$	~1520, ~1280, ~1180		—	

* R′, R″, R‴ = Alk; R = H or Alk; M^+ = cation. When electronegative substituents are present, the frequencies vary in conformity with Table 3 and Section VI.

Kamlet and Kaplan[236] ascertained by means of infrared spectroscopy the presence of a dinitromethyl anion in a Michael reaction product of unknown structure. Lindenmeyer and Harris[237] detected a low-temperature isomorphous transition in crystalline tetranitromethane.

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In conclusion the Reviewer would like to emphasise yet again the variety of problems and methods of attack in establishing the structure and mutual influence of atoms and groups in nitro-compounds which have been solved by means of infrared spectroscopy. The range of problems begins with establishing the structure of unknown compounds, investigating the effects of conjugation and dissociation processes, and terminates in studying the fine structure of nitro-carbanions and analogues of aci-forms, investigating the specific interaction of anions with the solvent, etc.

The advances made in the technique of obtaining infrared spectra—the use of such acid-stable optical materials as germanium, the improvement of instruments, increase in their accuracy and extension to longer wavelengths of the spectral range recorded—all this considerably broadens the already great possibilities of infrared spectroscopy for solving theoretical and practical problems in organic chemistry.

Table 6 gives the regions of vibration of the nitro-group which are suitable for the identification of nitro-compounds of unknown structure.

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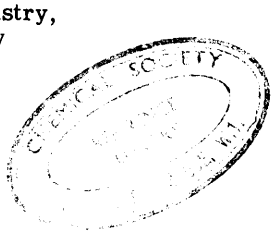

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Chromatography of Carbohydrates on Ion-exchange Resins

Yu.S.Ovodov

The literature data dealing with an effective method for the analysis of a mixture of carbohydrates using ion-exchange resins are reviewed. The separation of carbohydrates by this method is based on three main principles: (1) ion exchange; (2) adsorption and gel filtration; (3) partition chromatography. The use of ion-exchange resins yields clear cut qualitative and quantitative results and the analytical process may be automated. The method is distinguished by higher reliability and sensitivity and satisfactory reproducibility.
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I. INTRODUCTION

One of the main problems in carbohydrate chemistry is the separation of complex mixtures of mono- and oligosaccharides and the identification and quantitative determination of their components. A wide variety of chromatographic methods are employed for the solution of this problem. Here mention should be made primarily of paper chromatography[1,2], partition column chromatography on cellulose[3], adsorption column chromatography using a mixture of charcoal and zeolites[4], and gas–liquid chromatography[5–8]. Thin-layer chromatography of carbohydrates[9,10] is less widely used, although in many cases it yields good results[10]. It is also interesting to note that considerable advances have been achieved at the present time in the separation and quantitative determination of carbohydrates by chromatography on ion-exchange resins, although this method has not yet attracted the attention that it deserves. The separation of carbohydrates on ion-exchange resins depends on three different processes: (1) ion exchange; (2) adsorption on ion-exchange resins; (3) partition between the aqueous phase of the resin and the organic stationary phase. Nevertheless in many cases only one of these plays a decisive role and one can therefore adopt a conventional classification of such separation into ion-exchange adsorption, and partition chromatography on ion-exchange resins and treat each separately.

II. ION-EXCHANGE CHROMATOGRAPHY

1. Chromatography on Neutral Carbohydrates

The method of ion-exchange column chromatography for the separation of neutral monosaccharides was first proposed at the beginning of the 1950's.[11,12] It is well known that borate ions react with carbohydrates containing vicinal hydroxy-groups with formation of negatively charged carbohydrate-borate complexes. It has been established that a quite satisfactory separation of the mixture of carbohydrates may be achieved on a highly basic anion-exchange resin, such as Dowex-1, when the chromatography is performed in borate buffers[11]. Mannose and fructose, arabinose and xylose, and sucrose and maltose have been separated by this method. However, it should be noted that the method suffers from the disadvantage of unduly large volumes of eluates (up to 1.5 litres), despite the fact that relatively small columns (0.5 × 11 cm) are employed. Subsequently various ion exchangers and modifications of the method were used for the chromatographic separation of the borate complexes of carbohydrates[12–20].

In 1959 Nakamura and Mori[13] described the separation of carbohydrates in 50% ethanol by ion-exchange chromatography using the above principles. In order to overcome the basic disadvantage of the method (large volumes of eluates), Hallén[14] eluted the resin with solutions at a higher ionic strength (0.01–0.03 M borax solution), the fractions being analysed with the aid of anilinium acetate[15]. The method is distinguished by high sensitivity (it is suitable for the separation and determination of microgramme quantities of the carbohydrate) and can be used directly for the quantitative analysis of the hydrolysates. However, unfortunately when this method is employed, satisfactory separation cannot be achieved in many cases. In particular mannose is eluted with lyxose, ribose with fucose, arabinose with galactose, and xylose with glucose. Attempts were made to improve Hallén's system by separating the borate complexes of neutral sugars at an elevated temperature (50°C), pH 6.8,[16] and using Dowex 2 × 8 in the borate-form. The fractions were analysed with the aid of anilinium acetate by a specially developed method[17]. The authors succeeded in achieving a satisfactory separation of a mixture of rhamnose, mannose, fucose, galactose, and glucose. This modification of the method is distinguished by satisfactory reproducibility, permits a quantitative analysis of hydrolysates, and has been successfully employed in the analysis of the monosaccharide composition of many glycoproteins[17]. Automatic analysis of eluates[18–20] and the use of a special anion exchanger[20] made it possible to overcome many disadvantages of the method and to achieve a separation of 12–15 mono- and oligo-saccharides. Ion-exchange resins have also been used to separate polyols, for which paper chromatography gives unsatisfactory results. The method of separation of polyols in the form of borate complexes on highly basic anion exchangers in the borate-form[21,22], which permits the analysis of fairly complex mixtures of such compounds, has been most widely used.

2. Chromatography of Acid Carbohydrates

Chromatography of acids derived from sugars on ion-exchange resins has been described in a number of publications[14,23-34]. Highly basic ion-exchange resins have been mainly used for this purpose. In view of the instability of uronic acids in an alkaline medium (particularly at elevated temperatures), high pH values must be avoided during chromatography. Dziewiatkowski[29] employed Amberlite IRA 401 × 2 (in the acetate-form) with a particle size of 200–400 mesh in a 0.9 × 36 cm column for the separation of uronic acids. The columns were eluted with an acetate buffer (0.1 M sodium acetate, pH 5.9) at a constant flow rate through the column (1 ml/5 min). Satisfactory separation of a number of uronic acids and the corresponding lactones was achieved. Even better results were obtained by Samuelson and coworkers[30,33] who employed Dowex 1 × 8 anion-exchange resin with very small and carefully fractionated particles (down to 13–17 μm) and eluted with acetic acid or sodium acetate solutions.

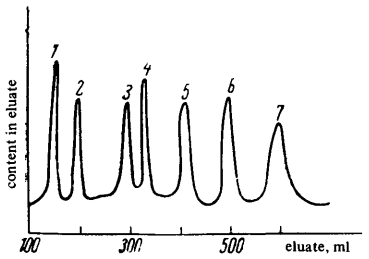

Figure 1. Chromatography of a mixture of uronic acids on Dowex-1 × 8 resin in the acetate-form (particle size 15–17 μm) in a 6 × 880 mm column; elution with 1 M acetic acid at 30°C at a rate of 0.97 ml min^{-1}; mixture components (1.5–2 μg each): 1) D-glucoheponic acid; 2) 6-β-D-glucopyranuronosyl-D-galactose; 3) D-galacturonic acid; 4) D-guluronic acid; 5) L-iduronic acid; 6) D-mannuronic acid; 7) D-glucuronic acid.

Best results were achieved with simultaneous elution by sodium acetate and acetic acid[30,31]. Satisfactory separation of a fairly complex mixture of uronic acids was then observed (Fig. 1). The use of very small particles of resin and their careful fractionation increases the column efficiency and leads to better separation. The time required to separate seven uronic acids is 10–11 h. To reduce this period, larger resin particles were employed. However this greatly impaired the results. Nevertheless, this procedure may be useful in many special cases, for example in the separation of a mixture of galacturonic and glucuronic acids[31]. In these studies the eluates were analysed by carbazole or dichromate methods. The carbazole reaction is known to give different colour intensities with various uronic acids, which permits a rapid identification of the peaks. The nature of the uronic acid may be inferred also from the ratio of the peak areas obtained in the carbazole and dichromate determinations. This quantity is constant and characteristic of different uronic acids.

In ion-exchange chromatography a fully defined elution sequence of the various components of the carbohydrate mixture is observed. Neutral monosaccharides, which are hardly separated under these conditions[34], are eluted initially, are followed by aldobiuronic acids, and finally by simple uronic acids, the elution sequence of which depends on many factors and cannot be predicted beforehand.

In order to separate aldobiuronic acids, we employed dilute sodium acetate solutions[30]. Then it was shown that the use of borax solutions as eluents greatly improves the separation of aldobiuronic acids[33]. The partition coefficients of all the uronic and aldobiuronic acids decrease very rapidly with the concentration of borax solutions.

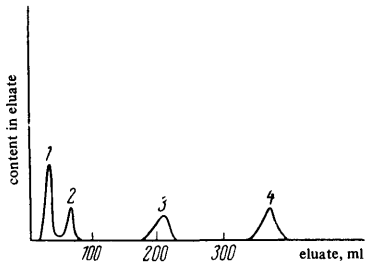

Figure 2. Separation of a mixture of certain aldobiuronic acids on Dowex-1 × 8 resin in the borate-form (particle size 23–25 μm) in a 3 × 870 mm column; elution with 0.12 M borax solution at a rate of 8.45 ml cm^{-2} min^{-1}; mixture components: 1) 4-*O*-methyl-α-D-glucopyranuronosyl-1→2-D-xylose; 2) α-D-galactopyranuronosyl-1→4-D-xylose; 3) β-D-glucopyranuronosyl-1→6-D-galactose; 4) D-glucuronic acid.

This is typical of hydroxyacids forming borate complexes[35], Therefore, in order to achieve rapid elution of the components, one may increase the borax concentration in the eluent solution. Fig. 2 presents as an example the separation of a mixture of certain aldobiuronic acids and D-glucuronic acid. Although carbohydrates are eluted in fairly diffuse bands, their separation is quite satisfactory. Knowledge about the borate complexes of hydroxy acids is very limited, but certain correlations between their positions on chromatograms and structures may be made. One of the rules states that the partition coefficients of hydroxyacids should increase with the number of free hydroxy-groups. Thus one must expect the earlier appearance of 4-*O*-methyl-D-glucuronic acid compared with D-glucuronic acid, which in fact does happen. Similarly, aldobiuronic acids are eluted more slowly than their methylated derivatives.

The study of the effect of the flow rate of the eluent solution on the separation of aldobiuronic acids showed that a sharp decrease of the flow rate leads to only a slight narrowing of the peak and therefore in the ion-exchange chromatography of aldobiuronic acids fairly rapid elution can be successfully employed.

When the temperature is increased, the separation is improved, but the degradation of aldobiuronic acids is at the same time accelerated appreciably. The use of an

automatic fraction analyser greatly accelerates and simplifies the process. In addition, automatic fraction analysis permits a more accurate determination of the peak positions on the chromatogram. It is then found that the deviation of the peak positions of uronic acids on chromatograms does not exceed 2%. The peak position characteristic of each acid can be successfully used for identification.

The separation of aldonic and aldobionic acids on anion exchangers has been described by Samuelson[36-39]. The method has been successfully applied to the analysis of sulphide liquors[41,42] and to the determination of terminal aldonic acid in cellulose[12] and hemicellulose[43].

In the elution by acetate solution a general tendency is observed in the series of hydroxyacids that for the same number of carboxy-groups acids containing more hydroxy-groups are eluted faster than those with fewer hydroxyls[44]. With few exceptions, this rule has been confirmed also in the series of aldonic and aldobionic acids[38,39]. The relation indicates that in this case the molecular size is the main factor determining the partition coefficient. An exception is mannonic acid, which is eluted with pentonic acids and D-glycero-L-mannoheptonic acid, which has a higher partition coefficient than many hexonic acids. These exceptions to the rules may be accounted for by the lower volumes of these hydrated anions, due to intramolecular hydrogen bonding, than for the other diastereoisomers.

From the practical point of view, it is interesting to note that the same elution sequence is reproduced also after prolonged operation of the columns. Anions differing in partition coefficients by 10% and more can be successfully separated. On elution by acetic acid and sodium acetate solution, the following relation between configuration and elution sequence is observed in the series of pentonic and hexonic acids: ribo-, arabo-, xylo-, lyxo-, the acids with the configurations at the beginning of the sequence being eluted earlier. Thus the position on the chromatogram can provide information about the structure of many aldonic acids and is of interest for their identification even when an authentic specimen is not available. As already pointed out, aldbiuronic acids are retained by the resin much less strongly than aldonic acids. On elution by sodium acetate, appreciable differences were observed between the partition coefficients of melibionic, lactobionic, and cellobionic acids, while the differences between cellobionic and maltobionic acids are insignificant[38]. In a borate medium aldonic acids are eluted in the following sequence: xylonic, arabonic, mannonic, gluconic, and galactonic[36,38]. Comparison of the results of chromatography in borate and acetate media shows that borate solutions are preferable for a complex mixture of aldonic acids; aldobionic acids are also satisfactorily separated. However, in a borate medium the latter are eluted almost simultaneously with aldonic acids. Therefore, when it is necessary to separate mixtures of aldonic and aldobionic acids, a preliminary separation of the acids into groups in an acetate medium is required, after which the borate method may be used to analyse the components in the individual groups. A promising method is chromatography on ion-exchange paper, which makes it possible to combine the useful aspects of ion-exchange and paper chromatography. The method has been successfully used by Oertel[25], who employed anion-exchange paper for the separation of uronic acids, lactones, and glucuronides and obtained a completely satisfactory result, despite the fact that the equilibrium between the acid and the corresponding lactone complicates the chromatographic pattern. One may also note the application of cation-exchange papers in the H^+-form for the separation of sugar acids[24]. However, in this case the ion exchanger plays the role of an acid, which is used in the developing systems in paper chromatography in order to avoid "tails". Thus the employment of ion exchange permits the analysis of mixtures of virtually any classes of mono- and oligosaccharides.

III. ADSORPTION CHROMATOGRAPHY

The results obtained by many investigators for the adsorption of polyhydric alcohols by ion-exchange resins[45-48] indicate that the latter may be used to separate carbohydrates by column chromatography. With increase in their size, the affinity of molecular for ion-exchange resins is reduced and thus large molecules are eluted first from the resin. This sequence breaks down, however, for methylated derivatives of carbohydrates, the most methylated derivatives being the last to be eluted by water from the columns[49,50]. The "molecular sieve" effect will also have an undoubted influence and therefore the percentage cross-linking in the resin and the salt form in which it is employed for chromatography are of definite importance. Both cation exchangers[49-55] and anion exchangers[56-58] have been used to separate mixtures of carbohydrates. Water was the eluent in all cases. Best results with cation exchangers were obtained on Dowex-50W (2–8% of divinylbenzene) in various salt forms. The barium-form[50] was used to separate monosaccharides. In one of our papers[51] the successful separation of D-xylose and L-arabinose on Dowex-50W (Ca^{2+}-form) was described. Mixtures of oligosaccharides or methylated monosaccharides have been separated with the aid of this resin in the lithium-form[52]. This form of the resin was also employed in the chromatography of a mixture of raffinose, sucrose, and glucose[49-52]. Satisfactory separation was then observed only for large differences in molecular weight and mixtures of carbohydrates with similar molecular weights could not be separated. More satisfactory results were obtained recently with the same ion-exchange resin in the potassium-form[53-55]. This method permits the fractionation of oligosaccharides in accordance with their molecular weights and the preparative separation of many mixtures with known monosaccharide compositions. Monosaccharides and their derivatives, particularly glucose and its mono- and di-isopropylidene derivatives, have been particularly satisfactorily separated. The use of anion exchangers did not show any advantages compared with cation exchangers. Reducing and non-reducing sugars have been separated on Amberlite IRA-400 (OH^--form) anion-exchange resin[56]. A mixture of raffinose, sucrose, and glucose have been fractionated on the basic forms of De-Acidite FF and preliminary separation of glycosides has been achieved on Dowex-1 resin[58].

The above method of fractionating mono- and oligosaccharides with the aid of ion-exchange resins is in many ways analogous to gel filtration on different types of Sephadex and biogels. The method is distinguished by rapidity and economy and constitutes a useful addition to other procedures for the separation of carbohydrate mixtures[55].

IV. PARTITION CHROMATOGRAPHY

A fundamental study by Samuelson and coworkers dealt with the partition chromatography of carbohydrates on ion-exchange resins. Preliminary studies of the sorption of monosaccharides and polyols from aqueous alcoholic solutions by ion-exchange resins[59-61] showed that the latter may be successfully employed for the partition chromatography of carbohydrates. The early attempts[62,63] gave promising results, after which the method was developed further during recent years.

Since the diffusion of carbohydrates within the resin particles is slow, very finely ground resins are employed for chromatography. The rate of sorption decreases rapidly with increasing concentration of ethanol, and therefore unduly high concentrations of the latter can lead to unsatisfactory separation. A decrease of the flow rate of the eluent solution leads to sharper peaks and the separation is appreciably improved. A higher rate of elution is permissible in the separation of small amounts of carbohydrates[64,65]. In partition chromatography on ion-exchange resins, monosaccharides are eluted before disaccharides and these in turn appear before higher oligosaccharides. Hitherto, in many studies on the partition chromatography of carbohydrates, highly basic anion exchangers with a styrene–divinylbenzene matrix (Dowex-1, Dowex-21, T4, T5B, etc.) have been employed in the sulphate-form with a wide variety of particle sizes. Thus, using a 10 × 840 mm column with Dowex-1 × 8 in the sulphate-form with a particle size of 45–75 μm and eluting with 74% ethanol, Samuelson and Swenson[64,65] successfully separated glucose and sucrose. In the separation of more complex mixtures, they employed stepwise gradient elution. Fig. 3 illustrates the separation of carbohydrates on molecular sieves by this method.

The use of a resin in the chloride-form[66] usually sharply impairs the results. Nevertheless mannose and xylose are satisfactorily separated in this case too. The chromatography of monosaccharides on highly basic resins in the bisulphite-form has been described in a number of papers[66,67]. The method ensures a satisfactory separation of ketoses from aldoses. The use of highly basic anion exchangers with more polar matrices has been described—in particular dextran containing quaternary ammonium ion-exchange groups has been employed[68]. In many cases this led to an improvement of separation but no fundamental differences were observed. Cation exchangers have also been successfully used in the partition chromatography of carbohydrates[69,70].

The fractions were initially analysed[64,65] by the phenol-sulphuric acid method and then an automatic fraction analyser began to be used[65,69,71,72]; part of the eluate and the reactants were then introduced into the analysing system, by a proportionating pump. Automatic analysis yields satisfactorily reproducible results.

In order to elucidate the possibility of separating the various carbohydrates, the positions of the peaks on the chromatograms are determined and the partition coefficients D_V are calculated[66]. Small variations in peak positions may be observed as a function of the rate of elution, the concentration of the eluent, and elution temperature. However, the relative partition coefficients of various carbohydrates depend to a lesser degree on the experimental conditions. Therefore in the identification of different carbohydrates, one may employ the ratios of their partition coefficients and the partition coefficient of any one monosaccharide chosen as a standard. The sorption of sugars by anion exchangers depends on many factors. One of these is partition between the water associated with the resin and the less polar eluent[59]. The effect of this factor should lead to an increase of the partition coefficient with increase in the number of hydroxy-groups and with decrease in the number of non-polar groups in the carbohydrate. One may then expect an increase of the partition coefficient in the series tetroses < pentoses < hexoses, and deoxy- and methylated derivatives should have smaller partition coefficients than the corresponding normal sugars. However, in addition to this factor, the interaction of the carbohydrate with the matrix and the ion-exchange groups of the resin, which may alter the above elution sequence[66], also plays an important role.

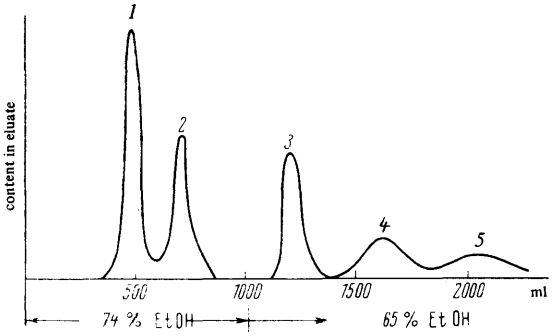

Figure 3. Separation of a mixture of carbohydrates in accordance with their molecular weights on Dowex-1 × 8 resin in the sulphate-form (particle size 45–75 μm) in a 10 × 840 mm column; gradient elution with alcoholic solutions at a rate of 0.8 ml min^{-1} cm^{-2} at 28°C; mixture components: 1) glucose; 2) sucrose; 3) raffinose; 4) stachyose; 5) verbascose.

Thus at the present time the elution sequence within each group of carbohydrates cannot be established *a priori* and is determined only empirically. It is noteworthy that in the majority of cases partition chromatography of carbohydrates and the ion-exchange resins gives a fairly satisfactory separation, which allows quantitative determinations. The sole factor which restricts the application of this method is the extremely low rate of diffusion within the resin particles. Therefore it is necessary to employ very small and as far as possible more porous particles. Thus, when a resin with a particle diameter of 45–75 μm is used, only partial separation of glucose and sucrose is observed, whereas particles with dimensions of 15–40 μm give a complete separation[73]. The employment of small particles permits the analysis also of monosaccharides[73] and it is possible to achieve a quantitative separation of mono- and oligo-saccharides[73,74]. The quality of the analysis depends to a considerable degree on the thoroughness of the fractionation of the resin. An increase of ethanol concentration also improves the results, provided that the consequent decrease of the rate of diffusion is compensated by a decrease of the resin particle size. In order to avoid under these conditions a sharp increase of column resistance to flow and to reduce the duration of analysis, the use of a mixture of an ion-exchange resin and Celite has been suggested[75]. It has been shown in a number of studies[66,69,70,72] that the partition coefficients of

the majority of carbohydrates in aqueous alcoholic mixtures differ appreciably. Fig. 4 presents the separation pattern for a mixture of twelve monosaccharides on an anion-exchange resin in the sulphate-form. The quality of the separation permits a quantitative analysis. The slight overlapping of the rhamnose and fucose peaks and of the arabinose and lyxose peaks does not affect the results of such analysis and, moreover, may be eliminated by increasing the concentration of ethanol or by increasing the column size. It has been established[76] that, in a quantitative determination of the monosaccharides present in wood hydrolysates, partition chromatography on anion-exchangers with automatic determination of the sugar concentrations in the eluates is a more convenient and accurate method than paper chromatography. The use of the orcinol method and careful fractionation of T5B anion exchanger (particle size 10–15 μm) in the sulphate-form permitted the development of an automatic micromethod for the analysis of a mixture of monosaccharides containing 6–30 μg of each component[77]. Partition chromatography on anion-exchange resins has been employed also for the separation of methylglycosides and methylated monosaccharide derivatives[78]. It was found that 94 wt. % ethanol, which ensures the complete separation of a number of the above derivatives, is optimum for elution[78].

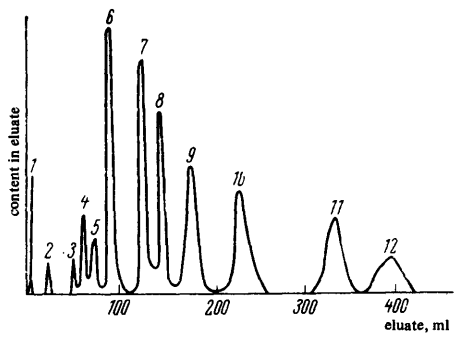

Figure 4. Analysis of a mixture of monosaccharides by partition chromatography on Dowex-21K anion-exchange resins in the sulphate-form (particle size 1–16 μm) in a 6 × 760 mm column; elution with 86% ethanol at a rate of 0.9 ml min^{-1} cm^{-2} at 75°C; mixture components (0.05–0.3 mg): 1) digitoxose; 2) 2-deoxyribose; 3) 2-deoxygalactose; 4) rhamnose; 5) fucose; 6) ribose; 7) lyxose; 8) arabinose; 9) xylose; 10) mannose; 11) galactose; 12) glucose.

Satisfactory separation of monosaccharides has been achieved on Dowex-50W × 8 cation-exchange resin with a very small particle size (14–17 μm) and elution by ethanol–water mixtures[69,70]. The ionic form of the cation exchanger has a marked influence on the partition coefficients. For monosaccharides, the latter increase in the sequence Li < Na < K. For all the sugars and all ionic forms of the cation-exchange resins, the partition coefficients decrease with increasing temperature. This finding accords with the results obtained on anion-exchange resins[71]. With small exceptions, the partition coefficients increase with the number of hydroxyls in the monosaccharide. A typical chromatogram is presented in Fig. 5, which shows that very satisfactory separation of seven different monosaccharides, including rhamnose and 2-deoxyglucose, which are not separated on anion exchangers in the sulphate-form, is achieved on a cation exchanger. Moreover, in contrast to anion exchangers, satisfactory results have been obtained for ketoses on cation exchangers. The lithium-form of the resin gives a better separation of deoxy-sugars than the sodium- and potassium-forms, but in work with the lithium-form a much higher pressure is required to maintain a constant rate of elution.

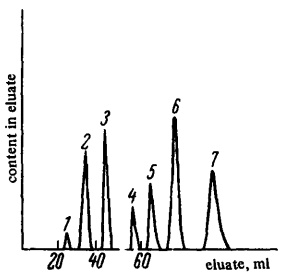

Figure 5. Separation of monosaccharides on Amberlite IR-120 cation-exchange resin in the Li^+-form; elution with 92.4% ethanol at a rate of 1.2 ml min^{-1} cm^{-2} at 75°C; mixture components: 1) 0.2 mg of rhamnose; 2) 0.4 mg of 2-deoxyglucose; 3) 0.6 mg of xylose; 4) 0.4 mg of arabinose; 5) 0.4 mg of tagatose; 6) 0.8 mg of glucose; 7) 1.5 mg of galactose.

One of the significant disadvantages of cation-exchange resins compared with anion exchangers is the poor separation of glucose and mannose. Partition chromatography has been successfully used also for the analysis of mixtures of polyols. Samuelson and Strömberg[79] suggested that in a quantitative determination of the components of such a mixture, they should be subjected to periodate oxidation with subsequent determination of the resulting formaldehyde with pentane-2,4-dione. The method permits an automatic fraction analysis, is distinguished by high accuracy and satisfactory reproducibility, and is suitable for microanalytical work. The subsequent application of the orcinol method, which does not give a colour reaction with polyols, and periodate oxidation permits the analysis of mixtures containing both aldoses and polyols. Various polyols are separated under the conditions already described for carbohydrates. A typical chromatogram obtained for polyols and aldoses on an 8 × 852 mm column with the highly basic T5B anion-exchange resin in the sulphate-form with a particle size of 3-17 μm is presented in Fig. 6. In elution with 86% ethanol at 75.5°C the duration of analysis is 11 h. Very satisfactory separation of the majority of polyols and aldoses is then observed, and only the peaks of dulcitol and mannitol overlap, which precludes an accurate quantitative determination of these polyols. The separation of mannose and dulcitol is also incomplete. To improve the results, elution with higher ethanol concentrations and longer columns are employed.

This leads to a complete separation of dulcitol and mannose, but the duration of analysis increases. To reduce the required period, very careful resin fractionation is necessary. As in the case of aldoses, the partition coefficients of polyols depend on the concentration of the alcohols and increase as it is raised, but the elution sequence is independent of alcohol concentration. A higher resin capacity leads to an increase of the partition coefficients and an improvement of separation. As for aldoses, the partition coefficients decrease with the number of hydroxyls in the polyols. The majority of polyols are eluted before the corresponding aldoses. Only ribitol and mannitol are exceptions.

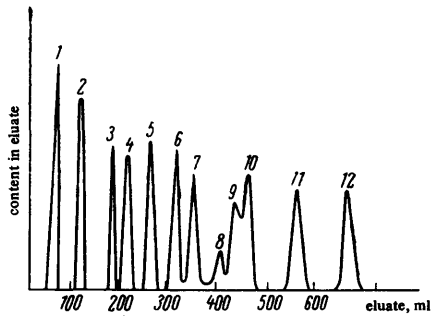

Figure 6. Analysis of a mixture of polyols and aldoses on TB resin in the sulphate-form (particle size 3–17 μm) in a 6 × 852 mm column; elution with 86% ethanol at a rate of 2.51 ml min^{-1} cm^{-2} at 75.5°C; mixture components: 1) glycerol; 2) erythritol; 3) xylitol; 4) arabitol; 5) arabinose; 6) xylose; 7) sorbitol; 8) mannose; 9) dulcitol; 10) mannitol; 11) galactose; 12) glucose.

Cation exchangers have also been used to separate polyols [70]. Resins in the lithium-form give the best results. Satisfactory separation of a complex mixture of polyols is also achieved in this case.

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Thus chromatography on ion-exchange resins permits a quantitative separation of very complex mixtures of monosaccharides and oligosaccharides. There is no doubt that the method will be very useful in the quantitative determination of the monosaccharide composition of a wide variety of carbohydrate-containing biopolymers, although the scope of the method as applied to the analysis of natural polysaccharides has so far been inadequately investigated [80, 81].

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Vitreous Carbon (Preparation, Properties, and Applications)

V.D.Chekanova and A.S.Fialkov

Vitreous carbon, one of the most important materials based on graphite carbon, is outstanding in its high mechanical strength, resistance towards aggressive media, and imperviousness to gases. Because of these unique properties, there has been a rapid growth in the range of articles made of vitreous carbon and in the number of applications.
The methods of production, formation mechanism, structure, properties, and the range of applications of vitreous carbon are described in this review. 97 references.

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I. INTRODUCTION

Modern technology has created a requirement for new constructional materials able to withstand high temperatures and aggressive media. One such material is artificial graphite. This material, however, though inert towards many reactive media, cannot be used at the boundary between two media because of its high permeability (due to the presence of a developed structure of pores and channels).

High-strength materials which are impervious to gases and liquids are urgently needed for a number of industrial applications. So far the need has been met by two materials: pyrolytic graphite[1] and vitreous carbon. These materials differ very substantially in their methods of preparation and in their properties: whereas pyrolytic graphite shows a marked anisotropy of thermal, electrical, and mechanical properties, vitreous carbon shows no anisotropy at all.

This review deals with the methods of preparation, the properties, and the fields of application of vitreous carbon.

Vitreous carbon is a new material, with a number of specific properties not found in the previously known modifications of carbon[2-4].

The study of vitreous carbon offers both practical and scientific interest, because this material is one of the non-graphitising forms of carbon, about which little is known.

II. PRODUCTION OF VITREOUS CARBON AND FABRICATION OF VITREOUS CARBON ARTICLES

Vitreous carbon and vitreous carbon articles can be produced by the thermal decomposition of some carbonaceous materials which give carbonised pyrolysis products without forming an intermediate liquid phase[5].

The first disclosure[6,7] of the production of an impervious form of carbon, using cellulose as the starting material, appeared in 1957. The process involved the following operations: preparation of an aqueous suspension in which the fibrous structure of cellulose is destroyed, precipitation of the product from suspension, and carbonisation with exclusion of air, followed by graphitisation[8-11]. Wheat-chaff cellulose, purified from lignin or xylan[6,12-15], may be used as the raw material for the production of impervious carbon.

Shortly after the first report of the preparation of this material, American, Japanese, French, and other papers discussed its properties and technical-scale production[6-17]. The raw material in this case can be synthetic resin of the resol (A-stage resin) or novolac (soluble phenol–formaldehyde) type[18,19], furfuryl alcohol or furfural[20-22], or polynuclear aromatic hydrocarbons[23,24]. The resins are carbonised with or without a catalyst by slow heating in a reducing or a neutral atmosphere[18,25,26].

Vitreous carbon can be prepared also from previously carbonised cellulose and synthetic resin, taken in the ratio of 3 : 7 by weight[27].

Some work has been done on the effect of filler additives to the cellulose dispersion[12]: the product was shown to remain impervious to gases even after the addition of fillers such as carbon black and colloidal graphite. The effect of the filler is largely dependent on the porosity and particle size of the filler itself. Thus, petroleum coke is too porous to be used as a filler for articles impervious to gases.

The addition of fillers can be a desirable step, since they do not degrade the high-temperature properties of the final product. Fillers lead to shorter production cycles, since they reduce the amount of material to be decomposed and the volume of volatile products evolved during the reaction.

A method[28] of production of vitreous carbon from furfuryl alcohol and furfural employs fillers of the same compounds, after hardening and crushing. This method evolves fewer volatile products, and the shrinkage of the manufactured articles is correspondingly reduced. The process is also cheaper, because hardening residues can be utilised.

Yamada and Takata[29] have proposed a method in which furfuryl alcohol or its initial condensation products are deposited in successive layers on the surface of a former, with or without the addition of carbon powder or chopped fibre. The resulting product is then graphitised or carbonised in the normal way. The advantage of this method is that volatile products are evolved more uniformly from the surface of the formed article during the hardening stage, and the quality of the product is thereby improved.

A preliminary degassing treatment of the components in vacuo is said[30] to improve the mechanical properties of the product, since it reduces the yield of volatiles during carbonisation.

Pyrolysis conditions (and in particular the rate at which the polymers are heated to the maximum temperature, and the time for which they are held at this temperature) can have a profound effect on the direction and the extent of the thermochemical reactions, and on the quality of the resulting non-porous material.

The technological production cycle of vitreous carbon occupies 2–4 months, the duration of the preliminary operations increasing in proportion to the maximum temperature which the vitreous carbon product is required to withstand[2].

Because of the extreme hardness of vitreous carbon, machining operations on the material are not straightforward, but they can be carried out with diamond-tipped tools, ultrasonic cutters, and grinding machines with carborundum wheels[2].

Most of the articles made of vitreous carbon do not require machining. The material is usually pressed to the finished size or cast into a mould[31] with allowance for shrinkage during heat treatment.

Tubular forms are made by the centrifugal forming method[32,33]. In one method of forming large cylindrical objects[34,35] the thermally reactive composition is cast into a former with a cylindrical core. Former and core are counter-rotated during hardening of the resin to avoid adhesion to the walls and to facilitate release of the article from the former.

Articles of many different shapes can be made of vitreous carbon: disks, tubes, cylinders, crucibles, beakers, boats, etc.[3] The maximum size of these articles which can be achieved in practice has been identified: in most cases the wall thickness is less than 3 mm. Tubes up to 1 m long and 40 mm in diameter have been made, as well as beakers of 3-litre capacity, disks up to 250 mm in diameter, and plates 100 × 500 mm. With especially close control over the composition of the resin, and the temperature and pressure during heat treatment, it is possible to make[25] rods 5–10 mm in diameter, articles with a wall thickness up to 6.3 mm, and crucibles up to 10 P in capacity.

In addition to articles of conventional shape, more unusual forms can be made of vitreous carbon: spheres 0.2–1.0 mm in diameter, tape weighing only a few mg per cm length, and vitreous carbon fibre[36-38]. The latter is made from furfuryl alcohol or furfural resin, which is hardened, drawn through a die under a pressure of 5 kg cm^{-2}, and carbonised in an inert atmosphere[39].

Vitreous carbon fibre has recently been prepared by extruding a mixture of resol, novolac, and furan resin (7 : 2 : 1 or 8 : 1 : 1 parts by weight), followed by rapid cooling, hardening, and carbonisation. Depending on the size of the orifice used for extruding the mixture, filaments 6–25 μm in diameter can be obtained[40].

The chemistry of vitreous carbon is the chemistry of the pyrolysis of synthetic resins. On heating a furfural–phenol–formaldehyde resin (FPFR), changes in weight and in composition are observed (Fig. 1 and Table 1)[41,42].

By monitoring the weight loss on heating, the thermal decomposition of the resin to the stage of carbonisation can be characterised. Heat treatment at 1200° gives an abundant evolution of pyrolysis products (low-molecular-weight gaseous species). The loss in weight under these conditions can be greater than 50%. On further carbonisation the weight change becomes insignificant and the weight curve runs parallel to the temperature axis.

The changes in chemical composition indicate a continuous succession of chemical reactions, the solid residue becoming gradually carbonised. On heating the resin at 1200°, the carbon content increases from 68.3 to 97.6% whilst the oxygen content decreases from 21.7 to 0.1%. The nitrogen and hydrogen contents decrease at the same time. However, the product which has been carbonised at 1200° still contains an appreciable amount of nitrogen (1.8%). Graphitisation gives an even purer carbonaceous material.

It has been found experimentally[41] that the insoluble fraction after heating FPFR to 100° amounts to 75%. On further heating the resin to 150°, the proportion of high-temperature compounds increases, and the insoluble frac-

tion becomes 95%. After treatment at a still higher temperature a completely insoluble polymer is obtained. The observed transition from a soluble to an insoluble polymer is evidence of chemical reactions within the material, confirmed by the change in free phenol and furfural contents during hardening of the resin. Thus, whereas a product containing 35% of free furfural and about 4% of free phenol is obtained after heating the material to 80°, no free components can be detected in the solid product after heat treatment at 200°.

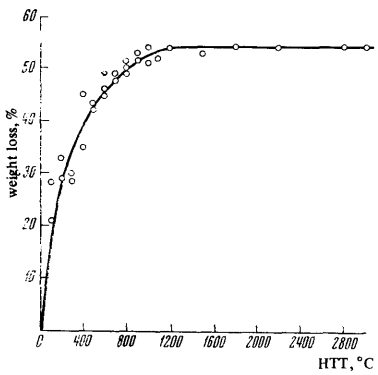

Figure 1. Change in weight of FPFR during heat treatment [42].

The greatest changes occur in the range 80–120°, and effectively cease at 180°. This is because the hardening process occurs mainly over the range 150–180° (as shown by chemical analysis).

Table 1. Composition changes during heat treatment of FPFR.

HTT, °C	Elemental analysis, %				HTT, °C	Elemental analysis, %			
	C	H	N	O		C	H	N	O
No heat treatment	68.26	5.68	4.40	21.66	500	82.39	4.65		
40	68.58	5.52			600	85.68	3.18	3.30	7.86
70	70.18	5.64	4.36	19.82	700	87.68	2.42		
80	70.16	5.59			800	91.29	1.52	2.84	4.35
100	70.88	5.61			1000	96.01	0.79	1.92	1.28
120	73.14	5.53			1100	96.98	0.53	—	—
150	73.24	5.50	4.54	16.72	1200	97.60	0.46	1.84	0.10
200	73.31	5.37	4.64	16.68	2000	98.29	0.23	—	—
300	74.33	5.40			3000	99.25	0.11	—	—
400	80.48	4.50	3.32	11.70					

The hardening process is controlled by a number of factors. In particular, the course of the hardening reaction is determined not only by temperature, but also by the heating rate and the duration of heat treatment. Higher heating rates tend to slow down the hardening process, to lower the proportion of insoluble fraction, and to increase the content of free components in FPFR. Polymers produced by heating the resin to 120° at different rates (1 and 30 deg h^{-1}) showed hardening factors of 89 and 81% respectively, and different contents of free furfural (5 and 10%) and of free phenol (0.9 and 1.3%). The experimental results of Fig. 2 show the variation of the degree of hardening with time of isothermal heating at different temperatures. The hardening time decreases on raising the temperature. Thus, a 10-hour heat treatment at 100° is needed to give 83% of insoluble fraction, as compared with only 5 h at 110°. Thus, the effect of temperature on the degree of hardening can be compensated to some extent by change in reaction time. The 150° curve is the steepest for times below 0.5 h and the flattest above 5 h. This shows not only that the reaction rate increases with hardening temperature, but also that the reaction at this temperature goes effectively to completion in a shorter time than at the other temperatures (120°, and below).

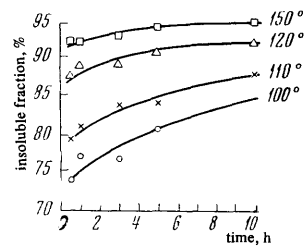

Figure 2. Percentage of insoluble fraction during hardening of FPFR under isothermal conditions [41].

An analysis of the volatile products evolved during hardening detected mainly furfural (95–96%), with a small amount of phenol, in the liquid condensate. The amount of condensate evolved is determined by the heating rate. Thus, on raising the rate from 10 to 40 deg h^{-1} the volume of condensate increases by a factor of 2 (from 20.8 to 42.2%). Hence we may conclude on the one hand that the heating rate determines the yield of polymer, and on the other hand that under these conditions the hardening of the material is due not only to chemical changes but also to the evolution of volatile fractions.

It is well known that many complex processes take place during hardening of phenol–formaldehyde resins [43]. Many workers believe [44–47] that a free-radical mechanism is involved.

The experimental results reproduced in Fig. 3 show the change in the concentration of paramagnetic centres (PMC) during hardening of the resin at temperatures up to 200°. The total number of PMC begins to increase appreciably at 70–80°, and continues to increase up to 120°. An arrest is observed over the range 120–150°, followed by a further increase in the number of PMC. The presence of a significant number of PMC in the original resin, decreasing during the initial heating period (below 70°) suggest that oxidation is occurring. This is confirmed by the fact that when the initial, pure novolac resin is allowed to stand in contact with the air for a long time its viscosity increases, and a fairly large ESR signal can be detected, whereas no such change occurs if the resin is stored out of contact with the air. The paramagnetism in this case may arise from peroxidic or quinonoid radicals formed by the oxidation of terminal groups of the resin molecule, which are also the most readily accessible to oxygen.

It should be noted that the hardened samples were very insensitive to atmospheric oxygen. The reported PMC concentrations relate to measurements in ordinary air.

It is evident from Fig. 3 that the number of PMC begins to increase when the temperature of heat treatment is greater than 70°, and becomes constant at 120–150°. On the other hand, chemical analysis indicates that the interaction between the components (i.e. the hardening process) continues to take place even in this range of temperatures. For example, the proportion of free phenol and furfural decreases gradually throughout the range of heat treatment temperatures. The i.r. spectra of the resin during hardening lead to the same conclusion. Experimental i.r. spectral data for the initial resin and for the material in various stages of hardening are shown in Fig. 4.

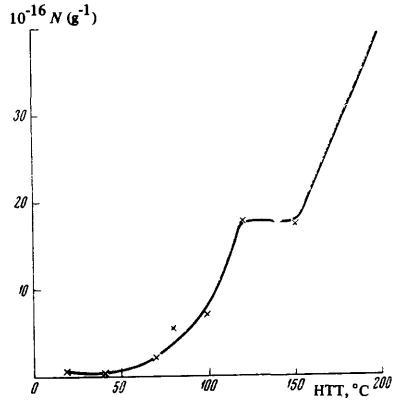

Figure 3. Formation of PMC during hardening of FPFR[42].

Heat treatment at 90° causes a large decrease in the intensity of the absorption band at 1660 cm^{-1} and almost complete disappearance of the 1570 cm^{-1} band. Both these bands arise from the furfural[48]: hence the changes may be explained either by a decrease in the amount of free furfural in the sample, or by volatilisation of this component, or by structural changes. The band at 1570 cm^{-1} is due to vibrations of the diene bonds in the furan ring which are conjugated with a carbonyl group. Hence, its disappearance may be ascribed to a decrease in the number of these bonds or to a decrease in the number of C=O groups (confirmed by the changes in the 1660 cm^{-1} band), or to the opening of one of the C=C bonds.

After heating the sample to 120°, the following changes are noted in the i.r. spectra. The band at 690 cm^{-1} (assigned to monosubstituted benzene rings, i.e. free phenol) disappears completely. The vibrations of the phenolic OH groups also give rise[49] to the bands at 1370 and 1200–1230 cm^{-1}, whose intensity decreases very significantly after heating the sample at 120°. The type of substitution of the benzene rings does not change (bands at 800–700 cm^{-1}), as shown also by the constant intensity of the 1600–1500 cm^{-1} bands which are very sensitive to the type of substitution. The number of aldehyde groups does not change (since the band at 1660 cm^{-1} is unchanged).

The absorption band of novolac at 1370 cm^{-1} is usually ascribed to vibrations of the phenolic hydroxyls. One of the furfural bands occurs at the same frequency. The 1370 cm^{-1} band disappears almost completely at 120°. It follows that the phenolic hydroxyls are involved in the hardening reactions. The nature of the bands in the 900–700 cm^{-1} region suggests that the benzene rings are not highly substituted[50,51]. No tetrasubstituted rings are detected by i.r. absorption. The narrow band at 880 cm^{-1}, which is characteristic of furans, shows that some of the five-membered rings survive the reaction.

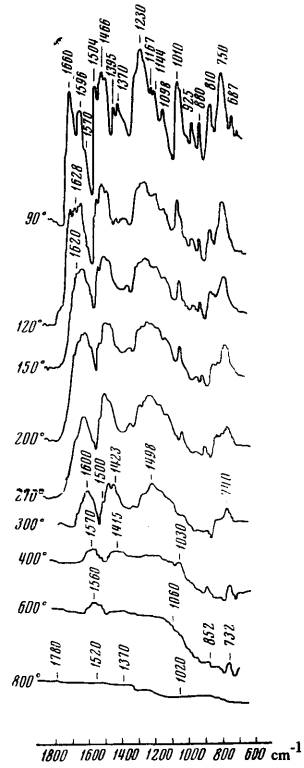

Figure 4. Infrared absorption spectra of FPFR after various stages of heat treatment[41,47].

A particularly interesting band, at 1628 cm^{-1}, can be due either to isolated C=C double bonds or to C=C double bonds conjugated exclusively with the carbonyl group or exclusively with the aromatic nucleus (without conjugation to another C=C bond).

After heat treatment to a higher temperature (150°), the absorption band of the aldehyde carbonyl group (1660 cm^{-1}) is no longer detectable. The strongest band is at 1620–1630 cm^{-1}. The 1370 cm^{-1} band (phenolic hydroxyls) has disappeared completely. The absorption bands associated with the furan ring are weaker, particularly the 930 cm^{-1} band from monosubstituted furan. Changes can be detected in the intensity of the 900–700 cm^{-1} band, and that of the 740–750 cm^{-1} band also shows a marked change. This latter band corresponds to the vibrations of the unsubstituted hydrogen in *ortho*-substituted benzene rings and in monosubstituted benzene and furan rings. The intensity

of absorption in the trough between the bands at 740 and 810 cm^{-1}, due to the formation of di-*ortho*-substituted rings, begins to increase at 150°.

The 1010 cm^{-1} band (from the C–O–C group) is the only furfural band still clearly visible in the spectrum at 200°. The 770 cm^{-1} band (triply substituted rings) is sharply resolved. At 870–880 cm^{-1} we observe a broad absorption band apparently due to the formation of 4-substituted benzene rings. The intensity changes in the region of 1600–1500 cm^{-1} are also interpreted in terms of changes in the type of substitution.

Thus, an analysis of these experimental results suggests that the hardening process occurs mainly in the range 70–150°, and that the process is characterised by a change in the number of PMC. The point at which the concentration of PMC begins to increase, and the point at which it becomes constant, can be identified with the initial and the final hardening temperature. The increase in the concentration of PMC is due to the formation of random molecular networks with a large number of broken cross-linking bonds.

The constancy of the concentration of PMC between 120 and 150° (Fig. 3) is evidently the result of the hardening of the resin to a solid product (of relatively low hardness). Isothermal heating in this temperature range produces only a slight consolidation of the three-dimensional network without forming any new PMC. These conclusions are consistent with the results of chemical analysis, which indicate that most of the free components of the resin have reacted chemically, and they are consistent also with the observed i.r. spectral changes.

In particular, the 1660 and 1370 cm^{-1} bands disappear almost completely at 150°. The most important band is found at 1620–1630 cm^{-1} (double bonds).

The increase in the concentration of PMC at temperatures above 150° is probably caused by pyrolysis of the resin.

The rate of hardening of the resin plays an important part in the formation of PMC. Thus, increasing the heating rate has been found to lower the concentration of PMC (from $\sim 2 \times 10^{17}$ spins g^{-1} at 5 deg h^{-1} to $\sim 0.7 \times 10^{17}$ spins g^{-1} at 20 deg h^{-1}). Evidently, a slow rise in temperature favours both a more complete chemical reaction between the components and the breaking of cross-linking bonds by pyrolytic action.

Isothermal heating at a temperature close to the upper hardening temperature does not alter the concentration of PMC appreciably. Thus, the number of spins was found to be 2×10^{17} and 2.5×10^{17} g^{-1} after heating at 120° for 1 h and 10 h respectively. These results are evidence that hardening occurs in a relatively short time.

The processes which occur during pyrolysis of hardened FPFR are particularly interesting[47]. The structural changes occurring during pyrolysis of the resin are reflected by changes in the i.r. spectra. It can be seen from Fig. 4 that heat treatment at 270° produces a sharp change in the intensity of the 1620–1630 cm^{-1} band. The band at 740 cm^{-1} becomes weaker, showing that the number of disubstituted rings has decreased. At the same time, sharp bands appear at 860 and 770 cm^{-1}, indicating more extensive substitution. The bands associated with the furan ring disappear, except the 1010 cm^{-1} band (C–O–C group). A band at 1260 cm^{-1} is clearly resolved in the region of 1200–1250 cm^{-1}. This band is found in all compounds containing C–O groups: it is often ascribed to aromatic ethers. Since the 1010 cm^{-1} band has not disappeared, any partial bonding of the C–O–C group (or –O–) to unsaturated carbon atoms should give rise to this band. It is difficult to account for the appearance of a broad line at 1600 cm^{-1}, and to decide whether this line is due to the aromatic ring only or whether it is conjugated with lines from C=C bonds.

At 300° all the furan bands have disappeared, including the 1010 cm^{-1} band. The i.r. spectrum now contains only bands associated with vibrations of aromatic rings (1600, 1500, and 740–800 cm^{-1}), and also bands from oxygen-containing groups (1250–1100 cm^{-1}).

After heat treatment at 400°, the oxygen content of FPFR is drastically reduced: all lines in the region 1250–1100 cm^{-1} have disappeared. The i.r. spectrum contains only an absorption band due to double bonds (mainly aromatic) at 1600–1500 cm^{-1}. The extent of substitution increases, as shown by the relatively strong band at 860 cm^{-1}. This effect may be due to condensation of the aromatic rings. The 1415 cm^{-1} band, due to residual $-CH_2$ groups, disappears completely at 600°.

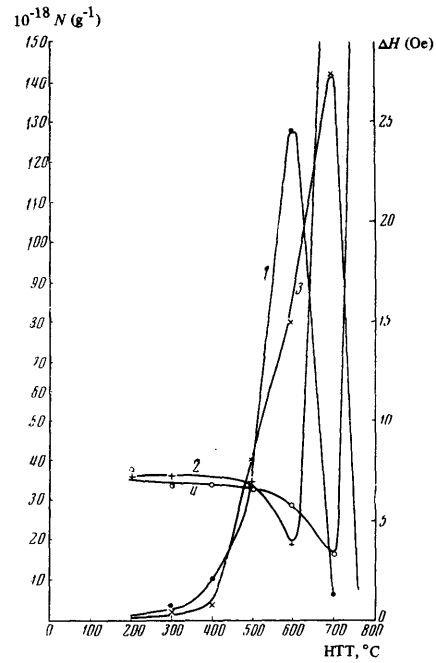

Figure 5. Concentration of PMC (N) and line width (ΔH) as a function of HTT[47]: *1*) and *3*) changes in N for samples heated at 5 and 20 deg h^{-1} respectively; *2*) and *4*) changes in ΔH for samples heated at 5 and 20 deg h^{-1} respectively.

The structural changes in the resin during heat treatment (HT) at temperatures above 200° (Fig. 5) result in changes in the concentration of PMC (curve *1*) and in the line width ΔH (curve *2*). The maximum ESR absorption is found at 600°, a temperature which is characteristic of carbonised substances. According to Trostyanskaya and coworkers[52], the highest concentration of PMC during pyrolysis of phenol–formaldehyde resins occurs in the range 400–500°. Others[53] have found a strong maximum at ~ 700° and smaller maxima in the region 1400–1800° and ~ 2800°. It follows that the position and the strength of the maximum are critically dependent on the type of resin.

The results of Fig. 5, obtained with samples in a vacuum, show that the total number of PMC increases slowly in the range 150–300°. Evidently, the growth in the concentration of PMC in this case denotes onset of pyrolysis, elimination of oxygen-containing groups and low-molecular-weight products, and dissociation of the dimethylimino bonds formed during the curing. The range 300–500° is characterised by a sharp increase in the concentration of PMC, due to the intensification of the above reactions and to the formation of aromatic molecules with unpaired electrons. This is confirmed by the analytical results (Table 1), which show that the most extensive changes in composition occur at temperatures ≥ 300°.

However, the carbonised product still contains a fairly large amount of nitrogen (1.8%) and a trace of hydrogen (0.5%). Thermal dehydrogenation, which sets in when the resin is heat treated above 400°, also contributes to the evolution of hydrogen from the sample (as shown by the results of chemical analysis). This process is partly responsible for the decrease in line width (ΔH) in the temperature range 500–600°, associated with the loss of hyperfine interaction (see curve *2* of Fig. 5). The main line-broadening mechanism in this temperature range, in addition to spin–spin interaction, is probably spin–orbit coupling, as suggested by the strong temperature dependence of the spin–lattice relaxation time. The spin–lattice relaxation time of a resin heat-treated at 600° is approximately an order of magnitude larger than for the same material at room temperature.

However, since the sharp rise in concentration of PMC is accompanied by a relatively small change in ΔH, it may be assumed that different types of paramagnetic centre exist in different regions.

The mechanism of thermal degradation of the resin has been elucidated by measuring the yield of gas as a function of temperature and time (Fig. 6). The composition of the gas is different for different temperature ranges. The strongest gas evolution occurs at 600–800°, the range where the degradation processes are most marked. On further raising the temperature there is a large decrease in the amount of gas evolved.

The degradation process begins to slow down after 25–30 min under isothermal conditions in the temperature range 200–1000° (Fig. 6).

The ESR absorption maximum observed at 600° corresponds with the temperature of maximum gas evolution (Fig. 5). This is evident from the composition of the gases evolved during pyrolysis.

As the pyrolysis temperature is raised, the composition of the gases evolved changes continuously (Table 2). The gas resulting from pyrolysis at 200–500° consists mainly of CO and CO_2. Significant amounts of methane are evolved at 500–800°, with a maximum at 600°, and at the highest temperatures the concentration of methane falls to 3%. The largest change was observed in the hydrogen concentration, which increased to 87% when the temperature was raised to 1000°.

Evidently, pyrolysis of methane can occur at the higher temperatures. The concentration of CO decreases continuously from 46 to 5%, and that of CO_2 from 52 to 3%.

The formation of volatile products by low-temperature pyrolysis is probably associated with the opening of heterocyclic rings, whereas at the higher temperatures (but below 800°) the mechanism is probably dehydrogenation of benzene rings.

The position of the ESR absorption maximum during carbonisation is determined not only by the type of resin but also by the heat-treatment regime. Fig. 5 shows the changes in concentration of PMC and in line width ΔH for a resin subjected to different heating rates (5 deg h^{-1} for curves *1* and *2*, 20 deg h^{-1} for curves *3* and *4*). It is clear that the concentration maximum and the ΔH minimum are shifted towards higher temperatures (> 700°) when the heating rate is changed from 5 deg h^{-1} to 20 deg h^{-1}.

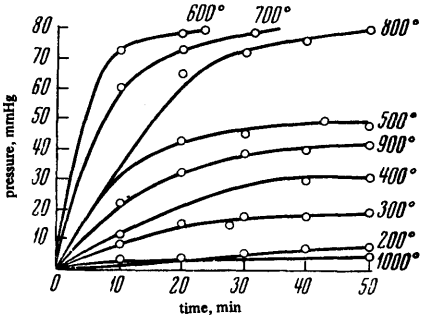

Figure 6. Yield of gas during pyrolysis of FPFR under isothermal conditions at different temperatures [47].

These effects can be understood on the assumption that bond breaking and thermal dehydrogenation (and the resulting structural rearrangements) cannot be fully effective if the heat-treatment temperature (HTT) is allowed to rise above 400° too rapidly.

Table 2. Composition of the gaseous pyrolysis products of FPFR [47].

HTT, °C	Components, expressed as vol.% of total gas evolved					
	CO	CO_2	CH_4	H_2	H_2O	Remarks
200	46	52	—	—	—	2% ($O_2 + N_2$)
300	59	37	—	—	—	4% ($O_2 + N_2$)
400	57	41	2	—	—	—
500	40	38	18	2	—	2% ethylene–ethane
600	19	10	45	26	—	—
700	17	2	38	43	—	—
800	8	2	20	68	2	—
900	6	3	5	84	2	—
1000	5	3	3	87	2	—

The decrease in concentration of PMC when the resin is heat treated above 600° is due to the loss of aromatic hydrogen and to the disappearance of free radicals which accompanies the formation of aromatic structures. The decrease in spin–lattice interaction time, leading to an increase in ΔH, is consistent with this hypothesis. The absence of ESR absorption for HTT > 700° (Fig. 5) is ascribed to incipient ordering of the resulting two-dimensional structure. As a result, the electrical conductivity of the sample begins to increase rapidly. It should be noted that the temperature at which ESR absorption begins to disappear is a characteristic of the particular resin: all the properties of the material begin to change at this HTT. Thus, the hardness and the density show a sharp increase, and the electrical resistivity begins to fall off very rapidly.

Studies of the influence of atmospheric oxygen on the PMC of a carbonised resin have yielded very interesting results. The relative sensitivity to atmospheric oxygen of the PMC in samples which have been exposed to different heating rates is illustrated in Fig. 7. Two regions where the effect of oxygen is large can be clearly seen. Thus, the ratio N_{vac}/N_{air} remains constant in both cases over the range 300–500°. The concentration of PMC also changes very little on heating the resin to 400°. This is because the rate of pyrolysis is very low in this range of temperatures, and the total number of PMC is small. The effect of oxygen becomes significant for HTT above 450°, and the maximum of the N_{vac}/N_{air} ratio coincides with the maximum PMC concentration in both cases. In both regions, the effect of oxygen is stronger when the sample is heat treated by the slower regime (Fig. 7). These experimental results justify the conclusion that the difference in sensitivity to atmospheric oxygen is associated with the extent of the structural changes in the resin, which are less extensive when fast heating rates are used. Hence, the PMC formed during fast heating of the resin are less sensitive to oxygen.

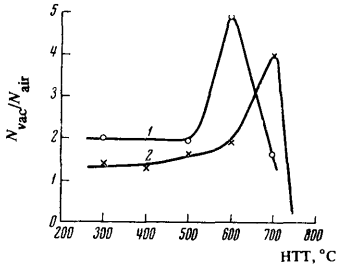

Figure 7. Relative sensitivity of the PMC to oxygen[47]: *1*) heating rate 5 deg h^{-1}; *2*) heating rate 20 deg h^{-1}.

The interaction of atmospheric oxygen with PMC is probably influenced by the oxygen chemically bound in the resin structure. For example, the fact that curve *2* in Fig. 7 has a lower maximum than curve *1* is probably explained by the presence of bound oxygen atoms in the pyrolysis products obtained at 600–700°. Even with the slower heat-treatment regime (5 deg h^{-1}), the products contain 7.86% of oxygen (Table 1). Oxygen atoms chemically combined in the carbonised samples can screen them from the effect of atmospheric oxygen.

Indirect confirmation of this hypothesis is provided by the measured spin–lattice relaxation times for pyrolysis at 600° (1.1×10^{-4} s for a heating rate of 5 deg h^{-1} and 0.12×10^{-4} s for a heating rate of 20 deg h^{-1}). It is well known that the presence of oxygen can lead to shorter relaxation times. The difference in the effect of oxygen on the PMC concentration for fast and for slow heating rates probably stems from differences in the degree of delocalisation of the unpaired electrons.

The presence of regions of different sensitivity may be partly due to the formation of different types of radical, with different reactivities towards oxygen, during the various stages of isothermal heating. This is confirmed by ESR measurements over a range of temperatures. For an HTT of 500°, corresponding to the onset of sensitivity to oxygen, the temperature dependence of the ESR absorption signal shows marked deviations from Curie's law.

III. PROPERTIES OF VITREOUS CARBON

1. Physical and Mechanical Characteristics

The properties of vitreous carbon of different origins (Japanese, French, and Soviet) are listed in Table 3[2–4,18,54]. The preparation of these materials is described in Ref. 55–59. The Table also lists, for comparison, the properties of a number of other materials: cellulose carbon, quartz, glass, high-density impregnated graphite, and ordinary graphite.

It is important to note that the properties of vitreous carbon can show wide variations, depending on the heat-treatment regime. Materials with different physical and mechanical characteristics can be prepared from a single carbonaceous starting material.

Vitreous carbon remains a solid up to 4000°K, and its properties are unchanged up to some temperature close to the sublimation point[60]. Its density is relatively low (up to 1.5 g cm^{-3}) in comparison with most refractory elements and compounds. Vitreous carbon is much harder than the common industrial grades of artificial graphite.

The elastic modulus of vitreous carbon is also higher than the modulus of the common graphitic materials (1500–3100 kg mm^{-2}, as compared with 300–800 kg mm^{-2} for industrial graphite).

The hardness of vitreous carbon is very sensitive to the maximum HTT of the material.

Kotlensky and Martens[61,62] showed, in their study of the mechanical properties of carbonaceous materials, that the strength of vitreous carbon (of any grade) is much higher than the strength of materials prepared from coke and pitch, but lower than the strength of pyrolytic graphite in a direction parallel to the deposition plane.

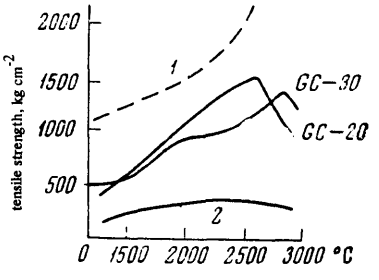

Figure 8. Tensile strength as a function of temperature[62]: *1*) pyrolytic graphite; *2*) graphitised material from pitch and coke. GC-20 and GC-30 are vitreous carbons heat treated at 2000 and 3000° respectively.

The strength of vitreous carbon is influenced by temperature (Fig. 8). The tensile strength of GC-20 vitreous carbon increases with temperature, reaching a maximum of 1400 kg cm^{-2} at 2500°.[62] At still higher temperatures

Table 3. Properties of different grades of vitreous carbon and other materials.

Property	Soviet vitreous carbon Ref.(18)			Japanese vitreous carbon Ref.(4)			French vitreous carbon Ref.(54)		Cellulose carbon tubes Ref.(4)	Transparent quartz Ref.(4)	Borosilicate glass Ref.(3)	Impregnated graphite Ref.(4)	High-density graphite Ref.(2)	Ordinary graphite Ref.(2)
	SU-12	SU-20	SU-30	GC-10	GC-20	GC-30	V 10	V 25						
Max. working temp. (°C) in an inert or reducing atmosphere or in vacuum	1200	2000	3000	1300	2000	3000	1000	2500	2500	1670	500	1300	3000	3000
Apparent density (g cm^{-3})	1.47—1.55	1.38—1.48	1.06—1.27	1.47—1.50	1.46—1.47	1.43—1.46	1.5—1.55	1.50—1.55	1.48	2.2	2.23	1.75—1.92	1.7—1.9	1.5—1.6
Open (apparent) porosity, %	0.2—1.3	0.7—2.0	1.8—2.2	0.2—0.4	1—3	3—5	0	0	—	—	—	8—15	10—20	25—35
Gas permeability (cm^2 s^{-1}) at room temperature	$\leqslant 10^{-8}$	$\leqslant 10^{-8}$	$\leqslant 10^{-8}$	10^{-11}—10^{-12}	10^{-10}—10^{-12}	10^{-7}—10^{-9}	$\leqslant 10^{-10}$	$\leqslant 10^{-8}$	10^{-12}	10^{-10}—10^{-12}	10^{-10}—10^{-12}	10^{-5}—10^{-6}	10^{-1}—10^{-2}	10^{0}—10^{-1}
Shore hardness	—	—	—	110—120	100—110	70—80	120—125	120—125	—	—	—	45—55	—	—
Microhardness, kg cm^{-2}	150—230	110—170	70—80	—	—	—	225	150—175	—	—	—		—	—
Bending strength, kg cm^{-2}	2600—3200	2100—2400	2100—2400	900—1000	700—800	400—500	1000	600—800	—	400—800	400—800	400—500	200—500	100—180
Electrical resistivity, ohm mm^2 m^{-1}	45—54	45—54	45—54	45—50	40—45	30—35	55	45	45	10^{19}	10^{11}	9—11	—	—
Ash content, %	0.01—0.05	0.01—0.05	0.01—0.05	0.1—0.2	0.1—0.2	<0.05	0.02	0.005	—	—	—	0.1—0.2	—	—
Thermal conductivity, kcal m^{-1} h^{-1} deg^{-1}	—	—	—	3—4	7—8	13—15	—	—	—	—	0.5—1.0	100—120	100—120	100—120
Thermal expansivity, $\times 10^6$ (deg^{-1})	4.6—5.8*	4.6—5.8*	3.7—5.7*	3.2—2.2	2.0—2.2	2—2.2	3.2	3.2	2.5	0.3	3.2	2—2.5	2—2.5	2—2.5
Elastic modulus, kg mm^{-2}	2800—3100	2300—2700	1500—1700	2700—3000	2500—2900	1500—2000	2850	2200	2700	7780	7000	1000—1200	500—800	300—600

* The measurements for grades SU-12, SU-20, and SU-30 were made at 1200, 2000, and 3000°C respectively.

the tensile strength begins to fall off, as in the case of most graphitic carbons prepared by traditional methods. In GC-30 vitreous carbon the tensile strength also increases as the temperature is raised from 1900 to 2700°, but it is lower than the strength of GC-20 over most of the range of temperatures. It is not clear from the data whether the tensile strength of GC-30 reaches a maximum at 2700° or whether it continues to increase with temperature.

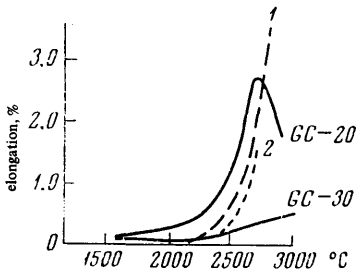

Figure 9. Elongation at break as a function of temperature[62]: *1*) pyrolytic graphite; *2*) graphitised material from pitch and coke. GC-20 and GC-30 are vitreous carbons heat treated at 2000 and 3000° respectively.

At temperatures of the order of 2200° and below the elongation at break of vitreous carbon (Fig. 9) is less than 3%, i.e. of the same order as for materials prepared from pitch and pyrolytic carbons. At 2500° the elongation of GC-20 increases much more drastically than that of the other materials. The increase continues as far as 2700°, and the elongation remains much greater than that of pitch-carbon materials and slightly higher than that of pyrolytic graphite. In GC-30 vitreous carbon the deformation at break is smaller than in GC-20 and other graphitic carbon materials.

Table 4. Properties of different grades of vitreous carbon before and after deformation.

Property	Grade GC-20		Grade GC-30	
	initial	deformed*	initial	deformed**
Density, g cm^{-3}				
In air	1.50	1.29	1.50	1.44
In light petroleum	1.68	1.82	1.68	1.66
Elementary cell parameters, A				
c	7.00	6.85	6.84	6.86
a	2.43	2.43	2.45	2.44

* Sample was deformed by 33% at 2700°.
** Sample was deformed by 65% at 2700°.

The properties of vitreous carbon before and after deformation are listed in Table 4. In contrast to the normal graphitic carbons, vitreous carbon has practically identical properties in different directions[15]. Nakamura and coworkers[63] conclude that vitreous carbon remains isotropic even when it contains small additions of natural or synthetic graphite.

Materials with graphite additives do not differ appreciably in density, hardness, and elastic modulus after heat treatment at 1300 and 2000°. Materials of the same grade, but heat treated at 3000°, have very different properties. A likely explanation is that the presence of graphite assists graphitisation at temperatures above 2000°.

Fischbach[64,65] studied the strength and elongation at break of vitreous carbon samples as a function of temperature, and found that an initially isotropic material becomes anisotropic after deformation. This suggests reorientation of the crystallites in a direction parallel to the strain axis.

Unlike silicate glasses, vitreous carbon has a very high thermal stability. No change could be detected after many fast heating and cooling cycles between 1700° and room temperature[22]. Similar results were obtained after ten cycles of instantaneous heating to 2000° in a stream of nitrogen and quenching to room temperature (after one minute) in carbon powder, and after five cycles of heating to 1000° and quenching in cold water[66]. In this respect, vitreous carbon is superior even to fused alumina.

2. Electrical and Semiconducting Properties

Vitreous carbon is an electrical conductor, but its resistivity is higher than that of the usual grades of graphite and of the same order as that of the carbon-black grades of artificial graphite.

Barykin and coworkers[27], and also a number of foreign workers[67,68], have studied electrical conduction in vitreous carbon and have observed semiconducting properties over a wide range of temperatures.

Yamaguchi[67] measured the Hall coefficient, magnetoresistance, and electrical conductivity of vitreous carbon as a function of heat-treatment temperature (from 1000 to 3200°) and at different temperatures (20, 77, and 330°K). Two types of sample were investigated: impervious (i.e. glassy) and porous (Fig. 10), both prepared from the same starting material. For low heat-treatment temperatures the Hall coefficient of both samples varied with HTT in the same way: it was positive for HTT around 1000°, it became negative (going through a minimum at ~ 1400°) on raising the HTT, and again changed sign becoming positive at ~ 1600° HTT.

In the region of high heat-treatment temperatures the two samples behaved differently: whereas the Hall coefficient of vitreous carbon increased with HTT up to 3200°, without going through a maximum, the Hall coefficient of the other type of sample went through a broad maximum at a heat-treatment temperature of ~ 3000°, and began to fall off beyond that temperature.

The Hall coefficient of both types of sample was much lower than typical values for graphitised materials over the whole range of HTT. At lower measurement temperatures the maximum in the Hall coefficient curve for the second type of sample was shifted towards higher HTT. The Hall coefficient of vitreous carbon was independent of measurement temperature over the whole range of HTT.

The variation of magnetoresistance with HTT was very different for the two types of sample. In vitreous carbon the magnetoresistance was negative, and decreased on raising the HTT. In the second type of sample the magnetoresistance became positive after going through a minimum, and continued to increase rapidly beyond that point.

From these results, the authors conclude[67] that the graphitisation tendency of the two types of sample is differ-

ent: whereas the second sample begins to graphitise at high HTT (~ 3000°), the vitreous sample shows no sign of graphitisation even at a HTT of 3200°.

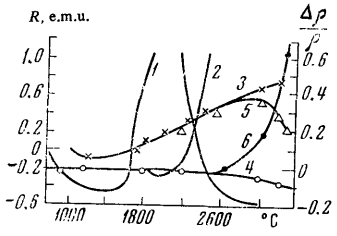

Figure 10. Hall coefficient (R) and magnetoresistance ($\Delta\rho/\rho$) as a function of HTT (measurements at 300°K)[68]. Samples of graphitising material: *1*) R, *2*) $\Delta\rho/\rho$; samples of the first type: *3*) R, *4*) $\Delta\rho/\rho$; samples of the second type: *5*) R, *6*) $\Delta\rho/\rho$.

Yamaguchi ascribes the inability of vitreous carbon to undergo graphitisation to specific structural features of this material. He believes that the second type of sample was structurally inhomogeneous, and that only some isolated regions of the material were able to undergo graphitisation.

Table 5. Pore size distribution in graphitic materials[16].

Material	Pore volume, Å	% or pores in range			Maximum pore size at pressure ≤ 1000 kg cm^{-2}, Å
		$7\cdot10^3$—$7\cdot10^4$, Å	$1\cdot10^3$—$7\cdot10^3$, Å	$1\cdot10^2$—$1\cdot10^3$, Å	
Ordinary graphite	32	27	4	3	$7\cdot10^4$
High-density graphite	11	3.5	1.5	6	$7\cdot10^4$
Impregnated graphite	5	—	2.5	2.5	$7\cdot10^3$
Vitreous carbon	0.35	—	—	0.35	$1\cdot10^3$

The thermoelectric power and Hall coefficient have been measured by Tsuzuku and Saito[69,70] as a function of measurement temperature and HTT. The observed change of the type of current carrier from holes (p-type) to electrons (n-type) and again to holes is interpreted in terms of Mrozovskii's σ-trap model of the electronic structure of the normal soft forms of carbon.

No definite theory of the electronic structure of vitreous carbon can be based on the above results.

3. Pore Structure

The microstructure of vitreous carbon differs drastically from that of graphite (both ordinary and impregnated[16]). The specific, granular pore structure of ordinary graphitised materials is not found in vitreous carbon.

The pore distribution in vitreous carbon, as measured with a mercury porosimeter, also differs from that of ordinary graphite (Table 5).

The most important characteristic of the new material is its low permeability to gases. Davidson[15] measured the permeability of cellulose carbon using tubular samples with 5.08 mm wall thickness. The samples were exposed externally to a helium atmosphere, the inner volume was carefully evacuated, and the tubes were connected to a diffusion pump and helium mass-spectrometer. The permeability of the material was well below 10^{-12} cm^2 s^{-1}. The permeability of vitreous carbon does not change with time: a diaphragm of this material mounted between a vacuum and helium at 1 atm pressure did not change significantly in the course of 700 hours. Other experiments showed that the material remains impervious at elevated temperatures (1000°).

The permeability of vitreous carbon can also be investigated by the density method. An impermeable material should have the same density in different media.

Table 6 lists the measured densities of vitreous carbon for different heat-treatment temperatures and in different media. Density was measured by the ordinary pyknometric method, and also in mercury and in helium[15].

Table 6. Density of vitreous carbons with different HTT in different media[20].

Heat-treatment temp., °C	Density, g cm^{-3}		
	pyknometric	in mercury	in helium
950	1.55	1.53	1.95
1200	1.61	1.59	1.66
1500	1.58	1.58	1.61
2000	1.55	1.56	1.58
2500	1.48	—	—

It is clear from the results of Table 6 that after heat treatment at 950° the pyknometric density of vitreous carbon (1.55 g cm^{-3}) is not the same as the density measured in a helium pyknometer (1.95 g cm^{-3}). The higher value of the density against helium suggests the presence of open pores.

Further heat treatment of the vitreous carbon causes the helium density to decrease to the level observed in the other media, i.e. it produces a closed pore structure. It is assumed that the formation of an isolated pore structure is due to the growth of separate crystallites during heat treatment (the pore diameter being small and comparable with the size of the crystallites). Diaphragms are formed within the pores, and the material becomes impervious to gases.

Intensive studies of helium density as a function of heat treatment temperature and X-ray studies by the low-angle scattering method have shown that the pores in vitreous carbon have extremely small dimensions. By comparing helium density data with low-angle scattering data Davidson concludes[15] that the average pore diameter is ~ 20 Å.

4. Crystal Structure

X-ray analysis has shown that vitreous carbon is a typical non-graphitising material[3].

The crystals in vitreous carbon, ~ 100 Å in diameter, do not have three-dimensional order. The crystallites are separated by voids and by chains of atoms without any particular orientation[5]. The degree of graphitisation of

GC-30 vitreous carbon is about the same as in petroleum carbon heated to 1900°.

Whereas in graphitised materials the interplanar spacing decreases gradually to 3.35 Å as a result of heat treatment, in vitreous carbon this value is constant (3.4 Å) even when the graphitisation temperature is raised above 3000°. Crystallographic studies of the new material have shown that the final product does not contain any large crystals. Well developed crystals are very seldom found, and their diameter is usually no more than a few hundred Ångstroms, whereas the average crystal size in natural graphites is at least 1000 Å.[42]

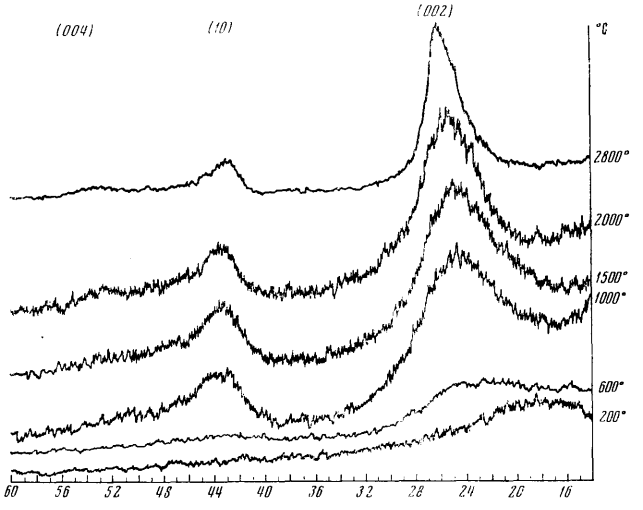

Figure 11. Diffractograms of carbonised FPFR products for different HTT[42].

X-ray diffraction patterns[42] for vitreous carbons heat treated at different temperatures are shown in Fig. 11. The diffraction patterns of the carbonisation products of the resin contain reflections of two types [(001) and (hk0)]. Diffuse (002), (004), (10), and (11) bands are observed in approximately the same angular position as the corresponding three-dimensional reflections from graphite. The (002) and (004) reflections arise from interference between groups of aromatic layers of condensed carbon atoms with sp^2 hybridisation of the valence electrons in the layer. The (10) and (11) bands are due to two-dimensional diffraction by flat layers[71].

A high background level is observed in the diffraction patterns of heat-treated samples. The large background arises from non-coherent scattering of the X-ray beams by carbon in non-aromatic configurations and by various radicals present as an amorphous phase.

On heating the starting material above 100°, complex structural changes take place. These consist mainly in breaking existing bonds and forming new ones, as shown by the diffraction patterns. At 200 and 600° the samples give an (002) diffraction line without a clearly defined maximum. The diffraction peaks from the (10) and (004) planes merge into a smooth curve, and cannot be resolved, suggesting lack of three-dimensional order. After heating at 1000° the (002) diffraction line is clearly visible, with a fairly sharp maximum. The asymmetric outline of the reflections indicates the presence of disordered networks in the heat-treated samples.

On raising the HTT, the following changes are observed: the layer spacing decreases, the layers of condensed aromatic carbon grow in size, the packets of flat hexagonal layers become thicker, and the proportion of amorphous phase decreases (Fig. 12).

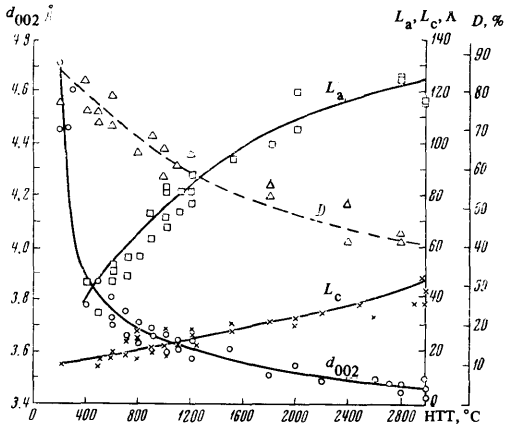

Figure 12. Interplanar spacing (d_{002}), crystallite size (L_a, L_c), and content of disordered phase (D) as a function of HTT in products obtained from FPFR[9].

The change of diamagnetic susceptibility of vitreous carbon with HTT also shows that this material is a typical non-graphitising carbonaceous material. Two regions can be distinguished in Fig. 13. For HTT between 200 and 1200° the diamagnetic susceptibility does not change very appreciably: it goes through an ill-defined minimum at 600–700°, and does not rise above the value -1.0×10^{-6} (CGSM units g^{-1}). At temperatures above 1300° the diamagnetic susceptibility begins to increase more rapidly, and the approximately linear increase continues up to 3000°.

The change in susceptibility with HTT in the low-temperature region is associated with changes in the molecular structure of the starting material, resulting from the polymer degradation processes. These processes involve the breaking of carbon–carbon bonds in macromolecules, and therefore give rise to a large number of unpaired, localised electrons. The appearance of unpaired electrons in a sample is detected as paramagnetism, due to the magnetic moments of these electrons, and this explains the decrease in the net diamagnetic susceptibility[72].

The fast growth of diamagnetic susceptibility at higher HTT is due to the increased size of the hexagonal carbon layers (not exceeding 150 Å, however). This is interpreted[73] as evidence of the end of the pre-crystallisation period. The diamagnetic susceptibility, unlike the susceptibility of well graphitised materials, does not saturate even at a HTT of 3000°. The susceptibility corresponding to this HTT is -5.1×10^{-6}, i.e. significantly different from the mean susceptibility of graphite (-7.2×10^{-6}).

The non-graphitising properties of vitreous carbon are probably due to the presence of a three-dimensional network of cross-linking bonds in the starting materials: this network hinders the rearrangement of structural elements which is the precursor of the formation of graphitic structures during heat treatment [74-77].

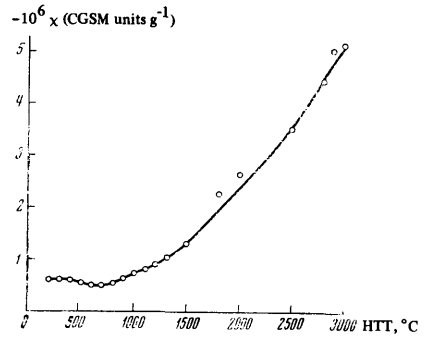

Figure 13. Magnetic susceptibility as a function of HTT [42].

As well as these purely structural effects, the presence of nitrogen atoms may affect graphitisation at temperatures above 1200°, because these atoms tend to hinder densification and the formation of ordered structures on heating.

Particles of different morphology have been detected in samples of SU-30 vitreous carbon by electron microscopy and selected-area electron diffraction [42]. Hence, graphitisation at high temperatures can take place heterogeneously, by evaporation and condensation of carbon atoms. The reason for the formation of morphologically different modifications in the products of high-temperature carbonisation is not clear.

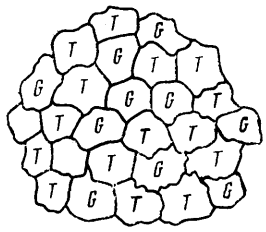

Figure 14. Structural model of vitreous carbon [77-79].

The regions of three-dimensional order, observed in microdiffraction experiments, must have a profound effect on the average structural parameters of the material.

Noda and Furukawa [78-80] studied the structure of vitreous carbon by measuring interplanar spacings, crystallite size, and the content of disordered regions, and also by radial distribution function analysis. Their results led them to a model of the structure of vitreous carbon involving two types of carbon: a tetrahedral modification, in which the arrangement of carbon atoms is similar to the diamond structure, and a trigonal modification, resembling graphite. The vitreous carbon may also contain carbon atoms with other types of bond.

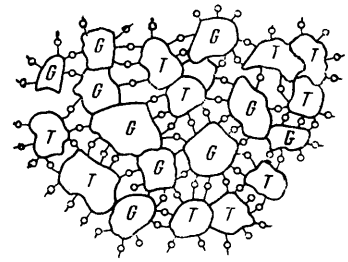

Figure 15. Structural model of vitreous carbon [77-79].

According to this structural model, the tetrahedral atoms (T) in vitreous carbon are responsible for most of the cross-linking bonds which hold together the graphitic layers (G) in a random arrangement (Fig. 14).

The model proposed for low-temperature grades of vitreous carbon, which are known to contain appreciable amounts of oxygen, involves oxygen bridges (Fig. 15) between T and T, T and G, and G and G regions.

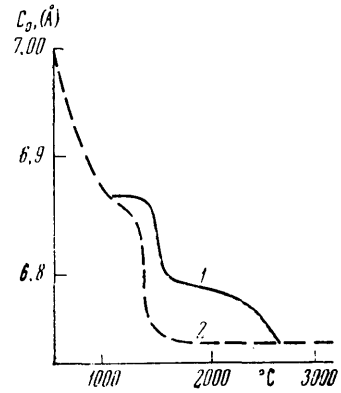

Figure 16. C_0 for GC-7 vitreous carbon (curve *1*) and for carbonised poly(vinyl chloride) (curve *2*) as a function of high-pressure HTT [81-83].

Kakinoki [81] suggests that the oxygen bridges can prevent the formation of ordered structures in vitreous carbon at temperatures up to 1200°, but they are broken down by heat treatment at 2500–3000°.

Noda and Cato [82,83] have shown that the dimensions of the crystal lattice in vitreous carbon can be modified by graphitisation under pressure. Fig. 16 shows the parameter C_0 of vitreous carbon (GC-7 grade) heat-treated under a pressure of 10 kbar and held at that pressure for 3 min.

For comparison, curve *2* gives the C_0 values for poly(vinyl chloride) carbon heat-treated under the same conditions.

The parameter C_0 falls to a very low value (6.72 Å) after heat treatment at 2600° under pressure. This low value of C_0 is not found in vitreous carbon prepared at ordinary pressure (C_0 for the GC-30 grade does not fall below 6.81 Å).

A possible explanation[84] is that the graphitic layers become mobile under pressure, and structural rearrangements towards more ordered structures become allowed.

In spite of the large number of published papers, our knowledge of the structure of vitreous carbon is still very inadequate.

5. Impurities in Vitreous Carbon

The specifications for construction materials used in many sectors of modern industry (nuclear energy, semiconductor technology, etc.) often include stringent purity requirements.

It is claimed[4] that the ash content of vitreous carbon does not exceed 0.02%. In the GC-30 grade, after additional purification, the ash content is decreased to ≤ 0.015%. Spectroscopic analysis results[2] for two grades of vitreous carbon (GC-20 and GC-30S) are summarised in Table 7. The following impurities are present: iron, aluminium, calcium, magnesium, silicon, vanadium, manganese, copper, and boron.

Table 7. Impurities in vitreous carbon[2].

Element	GC-20 before purification	$GC\text{-}30_S$	Element	GC-20 before purification	$GC\text{-}30_S$
Al	24.7	9.4	Mg	5.5	0.1
Ca	72.0	13.0	Mn	10.2	2.0
Co	none detected	none detected	Ni	none detected	2.6
Cr	none detected	none detected	Si	27.3	0.1
Cu	10	4.9	V	53.0	none detected
Fe	>100	>100	B	1	0.1

The impurity content of vitreous carbon is largely determined by the purity of the raw materials and by the temperature of heat treatment.

Lewis and coworkers[85] prepared semiconductor materials in containers made from vitreous carbon and from artificial graphite, and concluded that vitreous carbon is the better crucible material because it does not offer an open pore structure for the migration of impurities. Thus, the impurities present in vitreous carbon are less likely to contaminate the contents of the crucible than the impurities present in graphite.

6. Chemical Stability and Reactivity

Vitreous carbon is very stable towards many aggressive media. It is stable to fused alkalies and salts (sodium hydroxide, potassium bisulphite, calcium fluoride), acids (hydrochloric, hydrofluoric, nitric, sulphuric, chromic), and oxidising agents (bromine, chlorine, and mixtures of hydrogen peroxide and nitric acid and of nitric acid and potassium chlorate)[86,87]. Vitreous carbon is unaffected after two months in a mixture of concentrated HCl and HNO_3, which is known to disintegrate ordinary graphitic materials after 48 h at room temperature. The weight loss in mixed acids is acceptably low (see Table 8).

Outstandingly good anti-corrosion properties were reported also for vitreous carbon in contact with a mixture of nitric and hydrofluoric acid. However, vitreous carbon disintegrates in the presence of alkali metals. The behaviour of various grades of vitreous carbon in the presence of potassium vapour was studied by Halpin and Jenkins[88], who observed the formation of intercalation layers. Sodium vapour also caused disintegration of the vitreous carbon, but only at higher temperatures and with finely divided materials.

Table 8. Weight changes of vitreous carbon in oxidising media[66].

Oxidiser	Weight loss (%) after 50 days at 20 ± 5°		
	GC-10	GC-20	GC-30
98% H_2SO_4 + 60% HNO_3 (1:1 by vol.)	0.12—0.18	0.19—0.27	0.8—1.1
20% H_2SO_4 + 20% HNO_3 (1:1 by vol.)	0.03—0.06	0.19—0.20	0.5—1.2
60% HNO_3 + 35% HCl (1:1 by vol.)	0.04—0.05	0.12—0.15	0.01—0.02
20% HNH_3 + 20% HCl (1:1 by vol.)	0.03—0.10	0.12—0.14	0.05—0.06

Experiments on the interaction of vitreous carbon with fused alkali metal salts have shown that the extent of disintegration depends on the temperature and on the nature of the corrosive agent[89].

The oxidation of vitreous carbon by carbon dioxide has been studied in detail[7,90,91] because of its relevance to the use of vitreous carbon in CO_2-cooled atomic reactors. The conclusion was that vitreous carbon oxidises at about the same rate as reactor graphite if due allowance is made for the active surface areas of the two materials. This quantity depends on the parameters which determine the surface-to-volume ratio.

Table 9. Rate of oxidation of vitreous carbon in carbon dioxide[2].

HTT of vitreous carbon, °C	Experimental temp., °C	Gas pressure, atm	Rate of oxidation $\times 10^6$, $g\,g^{-1}\,h^{-1}$
2000	545±10	0.82	0.31
2300	545±10	0.94	0.27
1455	740±5	1.2	23.8
1620	740±5	1.12	6.6
1780	740±5	1.43	6.3
2000	740±5	1.05	3.0
2400	740±5	1.26	1.1
2010	785±10	0.49	1.79
2400	785±10	2.11	6.9

The rate of oxidation is affected by the gas pressure and by the temperature of heat treatment: it increases on raising the gas pressure and on lowering the HTT (Table 9). Addition of CO to the reaction medium lowers the rate of oxidation.

On raising the HTT from 1455 to 2400°, the reactivity of the vitreous carbon at 740° fell from 23.8×10^{-6} to 1.1×10^{-6} $g\,g^{-1}\,h^{-1}$. The reactivity decreases also at lower experimental temperatures.

Lewis [90] investigated the oxidation of vitreous carbon and pyrolytic graphite in different gases. The flow rate of the oxidising gas was 0.5 litre min^{-1} at temperatures below 800° and 1–1.5 litre min^{-1} above 800°. He concluded that vitreous carbon oxidises more slowly than various forms of pyrolytic graphite (Fig. 17).

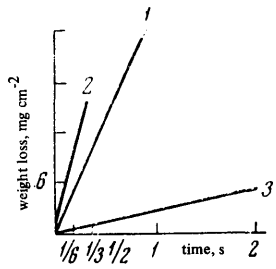

Figure 17. Weight loss of various graphitic materials as a function of time of oxidation in dry air at 750° [90]: *1*) purified graphite; *2*) not purified; *3*) vitreous carbon.

Yamada and Sato [16] studied the oxidation of vitreous carbon samples (15 × 15 × 1 mm) in a flowing mixture of nitrogen and oxygen in the ratio of 81 : 19 (by volume)at a temperature of 800 ± 5° and a flow rate of 0.5 litre min^{-1}. The results (Table 10) show that vitreous carbon is more stable towards oxidation than the other forms of graphitic material.

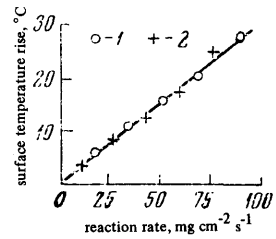

Figure 18. Rise in surface temperature as a function of rate of oxidation: *1*) vitreous carbon; *2*) graphite [90].

Blackman [91] observed the formation of isolated depressions on the surface of pyrographite and vitreous carbon during oxidation. He suggested that these craters are associated with the presence of metallic impurities, which act as oxidation catalysts, but this hypothesis is inconsistent with the finding of similar craters in vitreous carbon prepared from specially purified materials (ash content ~ 5×10^{-6}%). Heat treatment in a stream of pure argon at 800–900° was found to lower the reactivity of the vitreous carbon samples. High-temperature treatment in argon is known [90] to lower the concentration of active centres, possibly by the removal of surface contaminants.

Lewis measured the activation energy for the oxidation of vitreous carbon and other graphitic materials at various temperatures by plotting the logarithm of the reaction rate against reciprocal absolute temperature (Arrhenius curves). The activation energy for the oxidation of vitreous carbon by dry air in the temperature range 600–800° was found to be approximately 43 kcal $mole^{-1}$. On adding 26 vol.% of water vapour to the air the activation energy fell to 31 kcal $mole^{-1}$, and the oxidation rate could either increase or decrease. The activation energy for the oxidation of graphite in moist air fell from 43 to 38 kcal $mole^{-1}$ in the same temperature range. On raising the temperature, the activation energy was found to increase. Among the explanations [90] which have been proposed are the influence of open pores, the accumulation of catalytically active contaminants at the surface of the vitreous carbon, and diffusion in the gas phase.

The oxidation of carbonaceous materials is accompanied by evolution of heat, which may result in an increase in the true reaction temperature. The magnitude of this effect increases with reaction rate. The variation of the rise in surface temperature of vitreous carbon and graphite samples with rate of oxidation [90] is illustrated in Fig. 18.

The rate of oxidation of vitreous carbon in argon containing carbon dioxide and water vapour varies linearly with temperature (900–1400°) and with the concentration of active impurities in the sample.

The mechanism of the oxidation of vitreous carbon has not been fully elucidated.

Grades of vitreous carbon prepared in the Soviet Union (by the present writers) have been found to be stable towards acids (HCl, HF, H_2SO_4), concentrated solutions of alkali (KOH), and bromine. However, our vitreous carbon, like other graphitic materials, is disintegrated (though to a lesser extent) by a mixture of concentrated H_2SO_4 + HNO_3 (1 : 1 by volume) and by chromic acid mixture (a 3% solution of $K_2Cr_2O_7$ in concentrated H_2SO_4).

Table 10. Oxidation resistance of graphitic materials.

Material	Time for specified weight loss (%), in min			
	70	80	90	100
Artificial graphite	68	95	110	140
Thermal graphite	120	138	175	230
High-density graphite	160	185	225	275
Vitreous carbon	205	225	270	365

The vitreous carbon prepared in the Soviet Union is also stable towards the following media: a) fused alkali metal chlorides (NaCl, KCl, etc.) saturated with hydrogen chloride, with pure hydrogen, and also at the interface between the melt and the gas phase at 800–1000°; b) a fused mixture of chlorides and fluorides of the alkali metals (NaCl, HCl, NaF) in the presence of argon and at temperatures in the range 800–1000°; c) a fused mixture of lithium and potassium chlorides in the presence of chlorine at 700°; d) a fused mixture of lithium and potassium chlorides containing uranium oxide chlorides; e) cryolite–alumina melts in an inert atmosphere at 960–1060°.

IV. APPLICATIONS OF VITREOUS CARBON

Vitreous carbon has an important future because of its unique properties (low permeability to liquids and gases, chemical inertness, high stability) and of its low electrical resistivity and high thermal stability in inert media.

Impervious carbon is an important material for the fabrication of cans for fuel elements in nuclear reactors[4,6,92].

The high chemical stability and low electrical resistance of vitreous carbon offer unique advantages in the preparation of electrodes for a variety of electrochemical purposes[93,94].

There are interesting prospects of applying vitreous carbon as a construction material for chemical plant designed to operate in aggressive media: reactive gases and liquids, fused metals and electrolytes, radioactive products[86].

The new material can be used to fabricate laboratory ware for the vacuum evaporation of metals (e.g. aluminium, gold), and for reactions in fused alkalies, in strong acids, or in fused metals (e.g. liquid bismuth)[5].

Apparatus made of vitreous carbon has many definite advantages over alternative materials (nickel, platinum, tantalum, glass, and silicon) for the zone refining of metals and for the preparation of specially pure compounds[76].

Corrosion-resistant coatings for a variety of articles can be made of vitreous carbon.

Because of its high purity, imperviousness to gases, non-wetting properties, and chemical inertness, vitreous carbon is ideally suitable for use as a "crucible" in semiconductor technology and in the optical industry (e.g. for the preparation of large single crystals of CaF_2 and MgF_2).[5]

The electrical resistivity of vitreous carbon is adequate for the fabrication of resistance heaters. Small-scale heater elements made of GC-30 vitreous carbon are becoming commercially available[25].

Vitreous carbon can withstand very high temperatures and is therefore used as a construction material for the production of silicon carbide and to handle liquid bismuth[2,5]. We may expect items currently made of high-purity molybdenum, quartz, pyrolytic graphite, fused alumina, etc. to be gradually replaced by vitreous carbon items[3].

Because of its high resistance to thermal shock, vitreous carbon can be used in high-temperature technology to fabricate sheaths for temperature measuring apparatus operating in aggressive media[2,5], and because of its high mechanical strength it can be used in abrasion-resistant articles such as dies[96] and components for handling piece-parts[3,5].

Addition of 0.5–1.0% of vitreous carbon to carbon powders for the production of electric carbon brushes has been found[97] to increase the service life of the product from 7300 to 11 500 h.

In addition to the above applications, vitreous carbon is beginning to find outlets in a great variety of industrial operations[25,54,76]. Surge arresters for the telephone network were tested under severe conditions and found to be very reliable. Vitreous carbon welding rods for spot-welding aluminium last longer than ordinary graphite rods. The material can be used for casting metallic articles in precision moulds, in the preparation of microphonic powders, and as a heat shield[76].

Thread guides of vitreous carbon, used in the yarn industry, overcome the problem of static electrification which arises when electrical insulators are used for the guides[76].

Vitreous carbon filaments may find applications in space exploration, in aviation, and in other fields of activity by virtue of their low specific gravity, high tensile strength, and high thermal stability.

Vitreous carbon made in the Soviet Union[18] have been very highly rated for use as electrodes in chloride and cryolite–alumina melts, and in mixtures of alkali metal chlorides and fluorides in an atmosphere of argon, hydrogen, chlorine, hydrogen chloride, and H_2 + HCl mixtures at temperatures up to 1000°. Vitreous carbon electrodes are indifferent to melts of lithium and potassium chlorides containing uranium oxide chlorides. Vitreous carbon electrodes are beginning to replace platinum electrodes.

The superiority of vitreous carbon over other graphitic materials is very evident even in containers for molten indium, which overcome the problem of metal "seepage" and give a purer product because they are free from open pores.

Vitreous carbon has been used in research on crystal growth by the electrolysis of molten salts.

Thermocouple pockets made of vitreous carbon have been thoroughly tested, with favourable results.

Because of the unique properties of vitreous carbon, a much longer service life can be confidently expected from articles and fixtures made of this material instead of ordinary graphite. The range of vitreous carbon articles which are becoming available, and the number of applications of the material, are continuously increasing.

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Carbonylation of Mono-olefinic and Monoacetylenic Hydrocarbons

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The review deals with catalytic reactions involving the carbonylation of monoacetylenic and mono-olefinic hydrocarbons by carbon monoxide.
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I. INTRODUCTION

Reactions involving the carbonylation of unsaturated compounds by carbon monoxide under conditions of homogeneous catalysis in the presence of Group VIII metals and their compounds or acid catalysts are of considerable theoretical and practical interest. They permit the synthesis of valuable products: alcohols, aldehydes, ketones, saturated and unsaturated mono-, di-, and poly-carboxylic acids, their esters, chlorides, amides and lactones, and quinones, [1-9]. Some of these reactions have been achieved industrially[10]. As a result of numerous studies, the optimum reaction conditions have been investigated in detail, active catalysts have been selected, and the compositions of the reaction products have been determined.

New catalysts based on Group VIII noble metals have been found in recent years and certain features of the carbonylation mechanism have been elucidated.

The review deals with the reactions of mono-olefinic and monoacetylenic hydrocarbons with carbon monoxide, with the exception of hydroformylation reactions, which were described previously[11].

II. CARBONYLATION OF MONOACETYLENIC HYDROCARBONS

Acetylenic hydrocarbons are carbonylated in the presence of Group VIII metal carbonyls and hydrocarbonyls according to the overall equation

$$RC{\equiv}CH + CO + HX \rightarrow CH_2{=}CH(R)C\langle^{O}_{X},$$

where HX is a compound with mobile hydrogen.

Acrylic acid was obtained from acetylene, carbon monoxide, and water; acetylenealdehyde and acetylenedialdehyde were not formed. When water is replaced by other compounds with mobile hydrogen (alcohol, mercaptans, ammonia, amines, or carboxylic acids), derivatives of acrylic acid (esters, thioesters, amides, and anhydrides) are obtained[7,12,13]. These reactions are used at present for the industrial manufacture of acrylic acid and its derivatives. $\alpha\beta$-Unsaturated carboxylic acids (the hydrocarboxylation reaction), their esters (hydroalkoxycarbonylation), and other acid derivatives were obtained in the carbonylation of acetylene homologues. The addition of elements of formic acid (H−COOH) to the triple bond took place in accordance with the Markovnikov rule[14]. α-Phenylacrylic acid and not cinnamic acid was obtained from phenylacetylene[12]. The reactions were carried out by stoichiometric or catalytic methods.

The stoichiometric method consists in the reaction of acetylene with nickel, cobalt, or iron carbonyls at a pressure of 1−10 atm and 30−85°C in organic solvents: alcohols, acetone, ethyl methyl ketone, dioxan, tetrahydrofuran (THF), ethyl acetate, pyridine, and anisole, containing an inorganic (HCl, H_3PO_4) or organic (acetic) acid[15-24]. The reactions can be represented by the equation

$$4C_2H_2 + 4C_2H_5OH + Ni(CO)_4 + 2HCl \rightarrow 4CH_2{=}CH{-}COOC_2H_5 + NiCl_2 + H_2.$$

The nickel salt formed is then converted into a hexamine salt, which is treated in dilute aqueous solution with carbon monoxide at 100°C and 100 atm with formation of nickel carbonyl.

Methyl, ethyl, butyl, phenyl, tetrahydrofuryl, α-decalyl and other esters of acrylic acid were synthesised in high yields by this method. The reaction is autocatalytic, the duration of the induction period depending on the structure of the initial acetylenic hydrocarbons, the solvent, the acid, and the reaction temperature[25]. If an additional amount of the reactant is added after the induction period, the nickel complex formed as an intermediate acts as a catalyst. The rate and mode of reaction are influenced by the addition of water, acid, or base, for example pyridine, and also by the solvent. In anhydrous solvents, vigorous hydrogenation takes place: NiCl is formed as an intermediate from $Ni(CO)_4$ and then reacts with HCl to give $NiCl_2$ and H_2. This results in a decrease of the amount of final product. In the absence of acid the reaction does not occur. The acid strength does not influence the yield of acrylic acid, but does affect the yield of its esters[2]. The presence of oxidants in the reaction mixture inhibits the reaction, while reductants do not affect it[25].

The carbonylation of phenylacetylene, hex-1-yne, and methylacetylene by stoichiometric amounts of $Ni(CO)_4$ has been investigated in detail[26-30]. The reactivity of acetylenic hydrocarbons decreases with molecular weight. The addition of acetylene itself sharply increases the rate of reaction of homologues and increases the yield of the final products. Disubstituted acetylenes formed substituted acrylic acids[26,31,32]. Ethyl α-phenylcinnamate was obtained from diphenylacetylene and ethanol in benzene,

while in dioxan the main product was 2,3,4,5-tetraphenylcyclopent-2-en-1-one together with the above ester[32]. In the latter case the reaction probably proceeds via bis-(diphenylvinyl) ketone with its subsequent Nazarov cyclisation[2]. The carbonylation of diphenylacetylene in saturated sodium hydroxide in methanol in the presence of an excess of $Ni(CO)_4$ takes place with formation of *trans*-α-phenylcinnamic acid and 1,2,3,4-tetraphenylbutadiene in 25 and 67% yields respectively. The source of carbon monoxide is the intermediate dark-red $[Ni_3(CO)_8]^{2-}$ anion[33]. When diphenyl- and dimethyl-acetylenes react with $Fe(CO)_5$ under ultraviolet irradiation, tetraphenylcyclopentadienone and tetramethylcyclohexadienone are formed respectively and are isolated as complexes with iron tricarbonyl[34-37].

It is suggested that in the stoichiometric method a carbonium ion, which is formed initially during the acid catalytic process, reacts with $Ni(CO)_4$. In this stage four CO groups are transferred by a series of $Ni(CO)_X-C_2H_2$ complexes[38]. When the reactant ratios are accurately regulated, only "catalytic" amounts of $Ni(CO)_4$ and HCl are required for the carbonylation reaction.

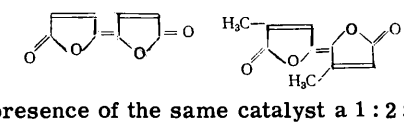
The carbonylation of acetylenic hydrocarbons by the catalytic method takes place at 150–200°C and about 30 atm in a homogeneous system containing 0.5–5% (relative to the solvent) of the catalyst, for which mainly complexes of Group VIII metals, and their halides, sulphides, carbonyls, etc. were employed[7,8,17,20,21,39-43]. Gaseous carbon monoxide is usually taken in an equimolar amount in relation to acetylene. Water, alcohols, tetrahydrofuran, pyran, dioxan, ketones, glycol monoethers, lactones, and *N*-alkyl-lactams are used as solvents[18,20,21,42,44]. Catalysts based on nickel have been investigated in greatest detail. The catalytic activity increases from the chloride via the bromide to the iodide, which, however, promotes also the acrylate polymerisation processes. The best catalyst proved to be $NiBr_2$, since it forms with carbon monoxide an unstable reactive complex NiCOBr, which readily gives up active carbon monoxide on regeneration of $NiBr_2$.[39,45] The active complexes are those of nickel, containing triaryl- or trialkylphosphines, trialkylstibines, and trialkylarsines, for example: $[(C_6H_5)_3P]_2.NiX_2.RX$, $[(C_6H_5)_3P]NiBr_2$, $[(C_6H_5)_3P]_2NiBr_2(C_6H_5Br)$, $[(C_6H_5)_3P]NiI_2C_6H_5Br$,[7,17,46-49] $(R_3P)_XNi(CO)_{4-X}$,[50] $NiBr_2[(C_6H_5)_3N(C_4H_9Br)]_2$, $NiCl_2[(CH_3)(C_2H_5)C_6H_5N]_2$, $[(C_6H_5)_3P.C_4H_9Br]_2C_5H_5N.NiBr_2$, $(C_6H_5)_3P(C_5H_5N.C_4H_9Br).NiBr_2$, $(C_5H_5N.C_4H_9Br).C_6H_5N.NiBr_2$,[51,52] $[(C_6H_5)_3P].[Ni(CN)_2]_3$,[53] $(R_3Sb)_XNi(CO)_{4-X}$,[54] $(R_3Sb)_2NiX_2$,[53,55-58] complexes of NiI_2 or $Ni(CN)_2$ and an alkali metal[59-61], complexes of $NiCl_2$ and acyclic and cyclic acid amides[62], halogen-containing organic complexes of phosphorus, arsenic, and antimony with carbonyl-forming substances[63,64], complexes of NiX_2 with oxygen-containing saturated heterocyclic compounds[64,65], a mixture of metallic nickel and nickel thiocyanate[58], metallic nickel on a carrier containing iodine[66], nickel halides on silica gel[67-75], nickel salts of naphthenic acids, nickel-dimethylglyoxime or a complex of $NiCl_2$ with 1-nitro-2-naphthol, and $NiBr_2$ complexes with ethanolamine, benzoxazole, and 1,3,4-thiadiazole-2,5-dithiol[76,77]. Metallic copper and mercury or their salts and also metallic nickel in an amount of 3–20% of the weight of the catalyst[76,78-81] and $HgCl_2$ (in the stoichiometric process) in an amount of 5–10% of the solvent[82] have been employed as activators of the carbonylation catalysts. The stability of the catalyst was increased by $CuSO_4$, antimony and arsenic chlorides, and hydroquinone[52].

The carbonylation of methylacetylene in the presence of $Ni(CO)_4$ yielded methyl methacrylate[83-85]. In the presence of methacrylic acid at 130°C and 13 atm the overall yield of methacrylic acid and its ester reached 85%. Methyl methacrylate was also obtained at 170–180°C and 10 atm when nickel halides, nickel complexes with $(C_6H_5)_3P$, and cobalt and chromium carbonyls were employed[85]. The side products of the reaction were methyl *trans*-crotonate, methyl isobutyrate, and acetone. Nickel and cobalt carbonyls showed the highest activity. In the carbonylation of butylacetylene in the presence of $[(XC_6H_4)_3P]_2NiBr_2$, where X = H, CH_3, or OCH_3, the activity of the catalyst increased when electron-donating substituents were introduced into the benzene ring of the ligand. The rate of reaction increased in the series X = H, CH_3, and OCH_3 and was proportional to the concentration of butylacetylene and the catalyst. The overall yield of esters was about 80%, the main product being butyl α-butylacrylate together with small amounts of butyl β-butylacrylate[86].

The rate of carbonylation of acetylene in a butanol–methyl acrylate solution at 30–75°C in the presence of $Ni(CO)_4$ depends on the partial pressure of carbon monoxide, being determined by the rate of diffusion of carbon monoxide, and decreases in the presence of an excess of acetylene greater than 40%. Above 75°C the rate of reaction falls by a factor greater than 2. An increase in the amount of the catalyst leads to the acceleration not only of the main reaction but also of the side processes, in particular the polymerisation of acetylene. Dilution of the initial acetylene–carbon monoxide mixture with nitrogen shortens the induction period, and, when the supply of hydrogen chloride is stopped, the reaction ceases rapidly. Cobalt and iron carbonyls are inactive under these conditions[25]. The solvent and the overall pressure have little effect on the rate, but affect significantly the mode of reaction in the range 4–150 atm. In the presence of water the main acetylene carbonylation products were acrylic acid and in *N*-vinylpyrrolidinone the products were saturated dicarboxylic acids[24].

In the presence of cobalt carbonyls and water in a neutral solvent, succinic acid and its homologues are the main products from acetylenes, together with cyclopentanone and monocarboxylic acids[87-89]. Bifurandione is formed in acetone solution[90-93] and in methanol and water solution or in methyl ether the product is dimethyl succinate together with small amounts of methyl acrylate[94-96]. In the presence of cobalt catalysts a mixture of methyl esters of acrylic, succinic, and γ-hydroxypimelic acids and the trimethyl ester of ethanetricarboxylic acid were obtained from acetylene, carbon monoxide and methanol[95-97].

In contrast to the analogous reaction of olefins (see below), the carbonylation of acetylene takes place at a high rate also in the absence of halides and halogens[98]. In the presence of $Co_2(CO)_8$ at 120°C and 250 atm, *cis*- and *trans*-octa-2,4,6-triene-1,4,5,8-diolides were obtained from acetylene, carbon monoxide, and acetic anhydride and, when acetylene was replaced by $CH_3C{\equiv}CH$, the products were *cis*- and *trans*-2,6-dimethylocta-2,4,6-triene-1,4,5,8-diolides[93], which were oxidised to 2,6-dimethylsuberic acid[99]:



In the presence of the same catalyst a 1 : 2 : 1 acetylene–carbon monoxide–hydrogen mixture in an excess of ethanol under a pressure of 50–80 atm and at a temperature of 100–120°C, gives rise to a mixture of products

containing ethyl propionate, propionaldehyde, its acetal, and diethyl succinate and $\gamma\gamma$-diethoxybutyrate. When ethyl alcohol was replaced by isopropyl alcohol, a mixture of isopropyl $\gamma\gamma$-di-isopropoxybutyrate, succinate, and β-formylpropionate was obtained[98,100]. Acetylene, carbon monoxide, and water in the presence of cobalt hydrocarbonyl yielded hydroquinone[101]. The carbonylation of acetylene derivatives in non-aqueous media catalysed by iron carbonyls leads to the formation of cyclic compounds[102].

In the synthesis of acrylate esters from acetylene, carbon monoxide, and alcohols, nickel, cobalt, and iron halides deposited on silica gel are employed as catalysts. The activity decreases in the series Ni > Co > Fe and I > Br > Cl. The reaction conditions were milder and the yield of the ester higher the higher was the molecular weight of the initial alcohol. Nickel naphthenate on silica gel proved to be the best catalyst for the synthesis of acrylic acid itself[97-75].

The carbonylation of acetylene in the presence of ruthenium compounds {the carbonyls $Ru_2(CO)_9$ and $[Ru(CO)_4]_3$, the salt $RuCl_3$, chelate complexes of ruthenium with acetyl acetonate} takes place at 160°C in water, methanol, acetone, or dioxan with formation of hydroquinone and quinhydrone. The amount of catalyst is 1% of the weight of the solvent. The yield of hydroquinone, which reaches 65%, depends on the reaction temperature and the H_2O/C_2H_2 ratio, but is little affected by the partial pressure of carbon monoxide in the range 53–160 atm.[103-105] Hydroquinone and quinhydrone were obtained similarly using rhodium compounds: $RhCl_3$, $Rh(CO)_2Cl$, rhodium carbonyl, and chelate complexes with acetylacetonate[103-106]. However, in a silver-lined autoclave acetylene was converted in the presence of hydrogen chloride and small amounts of $RhCl_3.3H_2O$ into a mixture of acrylic and 3-chloropropionic acid chlorides[107].

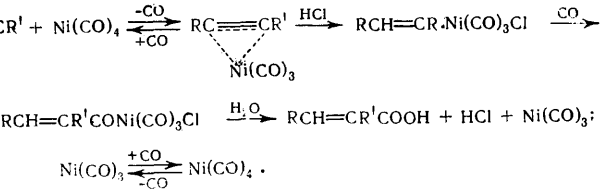
By reaction with $Rh(CO)_2Cl$ in benzene, diethylacetylene was converted into tetraethylcyclopentanephenol [tetraethylcyclopentanophenol ?], isolated as a complex with $RhCl_3$, and partly into 2,3,5,6-tetraethyl-1,4-benzoquinone, and diphenylacetylene was converted into 2,3,4,5-tetraphenylcyclopentadienylrhodium chloride and partly into hexaphenylbenzene[108] [wrong reference (Ed. of Translation)].

In the presence of palladium salts, the carbonylation of acetylene occurred under milder conditions: 60–125°C and 1–45 atm of carbon monoxide with formation of a mixture of saturated and unsaturated mono- and di-carboxylic acids. The butyl esters of acrylic, propionic, maleic, and fumaric acids were obtained in proportions of 24:9:38:10 from a 1:1 acetylene–carbon monoxide mixture in butanol containing 0.1% $CdCl_2$, 1.1% I_2, and 1.8% H_2O. An increase of the concentration of carbon monoxide in the mixture promoted an increase in the yield of the dicarboxylic acid esters. The replacement of I_2 by HI and of $PdCl_2$ by $PdSO_4$ did not influence the reaction. The addition of $SnCl_2.2H_2O$ inhibited the reaction[109].

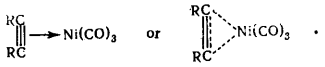
The carbonylation of acetylene in benzene solution in the presence of a $PdCl_2$ complex with dibenzonitrile proceeds with preferential formation of muconic acid chloride containing an admixture of fumaric and maleic acid chlorides[97,110,111].

In the presence of phosphine complexes of palladium, a specific role of the solvent was observed. In a 5:1 chloroform–alcohol mixture at 40°C and 1 atm, acrylate esters were formed. When chloroform was replaced by benzene, toluene, or xylene, catalytic activity was not shown below 80°C, which can be accounted for by the formation in the first case of the complex $Pd[(C_6H_5)_3P]_2.CHCl_3$ which is probably converted during the reaction into the hydride complex $Pd(H)Cl[(C_6H_5)_3P]_2$. A similar complex, obtained by the reaction of chloroform with $Pd[(C_6H_5)_3P]_4$, also catalysed the carbonylation of acetylene under analogous conditions[112].

The carbonylation of acetylenic compounds by the stoichiometric method may be represented by the following scheme[113]:

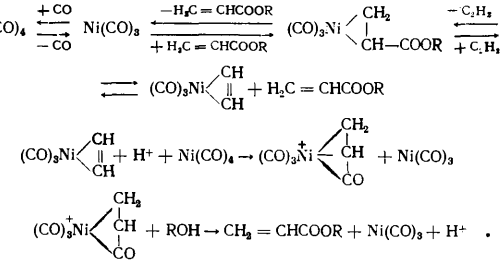


The acetylenic compound reacts with $Ni(CO)_4$ forming a π complex, which is converted under the influence of a proton into a σ-alkenyl and then alkenoyl organometallic compound:

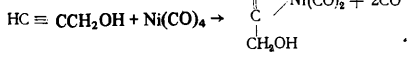


The complexes of nickel, cobalt, and iron carbonyls with acetylenic compounds are widely known. For example, $Co_2(CO)_9.C(C_3H_7)\equiv CH$, $Co_2(CO)_9C(CH_3)\equiv CH$, and $Co_2(CO)_9.CH\equiv CH$ were obtained from $Co_2(CO)_8$, CO, and acetylenic hydrocarbons at 70°C and 190 atm.[114-115]

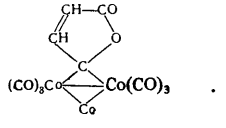
The carbonylation by the catalytic method has been represented by the following scheme[25,108]:



Thus $Ni(CO)_3$ is regenerated on formation of the reaction products. The dissociation of the metal carbonyl with simultaneous formation of coordination-unsaturated intermediates may proceed with the immediate evolution of two CO molecules, as was observed in the carbonylation of propargyl alcohol[108]:



Analogous intermediate complexes, which are of the type of π complexes of the catalyst and the substrate, were also formed in the case of cobalt, iron and other Group VIII metal carbonyls[115]. Cobalt carbonyl complexes with acetylene are known to be capable of reacting with several CO molecules under the conditions of the carbonylation reaction, forming complexes of the type



Such complexes may be converted further into dicarboxylic acids or into cyclic compounds[114,116].

Recently a major role in the carbonylation reaction has been attributed to hydrocarbonyls. It is assumed that nickel catalysts form in the first stage nickel hydrocarbonyl, which is in fact the true reaction catalyst[85]:

$$Ni(CO)_4 \underset{-nCO}{\overset{+HX}{\rightleftharpoons}} HNi(CO)_{4-n}X \xrightarrow{CH\equiv CR} CH_2=C(R)Ni(CO)_{4-n}X + RCH=CHNi(CO)_{4-n}X \xrightarrow{CO}$$
$$\xrightarrow{CO} CH_2=C(R)CONi(CO)_{4-n}X + RCH=CHCONi(CO)_{4-n}X \xrightarrow{R'OH} CH_2=C(R)COOR' +$$
$$RCH=CHCOOR' + HNi(CO)_{4-n}X,$$

where HX = H_2O, an organic acid, or an inorganic acid and R′ = H or alkyls.

The data presented in this section show that the carbonylation of monoacetylenic hydrocarbons leads to the formation mainly of $\alpha\beta$-unsaturated carboxylic acids, their esters, and other derivatives. The reaction proceeds in the presence of catalysts based on Group VIII metal carbonyls of hydrocarbonyls.

III. CARBONYLATION OF MONO-OLEFINIC HYDROCARBONS.

1. Reactions in the Presence of Catalysts Based on Group VIII Metals

The carbonylation of olefinic hydrocarbons[7,117] takes place under more severe conditions than that of acetylenic hydrocarbons: at 120–280°C and 100–300 atm of carbon monoxide in the presence of cobalt or nickel halides or carbonyls, sometimes activated by magnesium, aluminium, manganese, Cr_2O_3, tin, CuI, and RbI. Complex salts of the type $K_2[Ni(CN)_4]$, nickel and cobalt complexes of amines, and aqueous solutions of iron and cobalt salts of organic acids have also been used as catalysts. The results of earlier studies in this field are compiled in a previous review[1]. The carbonylation of olefins takes place on heating to 160–170°C in a mixture with a stoichiometric amount of nickel or cobalt carbonyl in the presence of water and acetic acid according to the mechanism

$$4RCH=CH_2 + 4H_2O + Ni(CO)_4 + 2CH_3COOH \rightarrow 4[RCH(CH_3)COOH + RCH_2CH_2COOH] + (CH_3COO)_2Ni + H_2 .$$

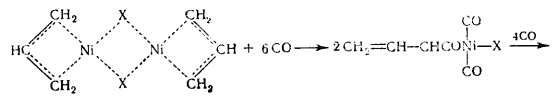
The principal characteristics of the carbonylation reaction are the same for both olefins and acetylenic hydrocarbons[7,98,117–120], certain reactive olefins, such as for example, bicyclo-[2,2,1]heptene, react under the same conditions as acetylenic hydrocarbons[121]. Straight-chain α-olefins enter into the reaction most readily with formation of a mixture of straight-chain and α-methyl-substituted carboxylic acids in proportions of 1 : (1.5–2.5) in the presence of nickel catalysts and 3 : 1 in the presence of cobalt catalysts[120–122]. Activators of nickel catalysts (I_2, HI, CH_3I, KI) accelerate the reaction and increase the yield of the straight-chain acids. In the presence of the $Ni(CO)_4 + NiI_2$ catalyst, C_2–C_4 olefins are converted into acids in yields up to 90%, which increase when solvents such as methanol, acetone, and dioxan, which readily dissolve both the olefin and water, are employed[119].

In the presence of $Ni(CO)_4 + NiI_2$, mainly propionic acid (85%) is obtained from ethylene, a mixture of butyric and isobutyric acids (48 : 52) from propene, a mixture of trimethylacetic and α-methylbutyric acids (60 : 40) from isobutene, and a mixture of caproic and α-methylvaleric acids from pent-1-ene. Qualitatively, the same acids are formed from β-olefins as from α-olefins. In the carbonylation of olefins, higher carboxylic acids, aldehydes, and polymers are formed as side products[120]. In the synthesis of butyric acids (yield 96%) from propene, carbon monoxide, and water, in the presence of $Co_2(CO)_8$, the reaction is of first order with respect to water, of zero order with respect to propene, and of a fractional order (0.6–0.8) with respect to the catalyst[122]. When water is replaced by methanol, butyric acid esters are obtained, whose yield increases with increase of carbon monoxide pressure from 25 to 208 atm, with increase of the catalyst concentration, and with decrease of reaction temperatures from 250° to 145°C.[123] The relative amounts of the isomers in the reaction products are influenced by carbon monoxide pressure, reaction temperature, and the nature of the catalyst metal: $Co_2(CO)_8$, $Ni(CO)_4$, or $Ru_3(CO)_{12}$.[124] In order to increase the catalytic activity, tributylphosphine[125] or small amounts of pyridine are added to $Co_2(CO)_8$. Pyridine accelerates the reaction and increases the yield of unbranched products[126–128]. The presence in the reaction zone of small amounts of H_2 does not prevent the formation of acids and their esters, but the hydroformylation of the olefins with formation of an aldehyde or an acetal takes place at the same time[129,130].

For the synthesis of propionic acid and its methyl and ethyl esters, nickel, cobalt, and iron halides deposited on silica gel (1 : 1), which proved more effective as a carrier than kieselguhr, pumice, and kaolin, are employed as catalysts. The catalysts can be arranged in the following sequences in terms of their activity[69–72,131]: Ni > Co > Fe and I > Br > Cl. It is suggested that the complexes $M(CO)I_2$, where M = Co, Ni, and Fe, are formed initially. They react further with carbon monoxide or methanol:

$$NiI_2 + CO \rightarrow Ni(CO)I_2 \xrightarrow[CH_3OH]{3CO} \begin{matrix} Ni(CO)_4 + I_2 \\ CH_3COOH + NiI_2 \end{matrix} \text{ etc.}$$

The iodides form complexes more readily than the bromides and chlorides. The stability of the complexes $M(CO)I_2$ obtained from the halides and carbon monoxide under pressure[39] decreases in the series Fe > Co > Ni, in opposition to the catalytic activity series[132]. When carbon monoxide was passed through solutions of π-allylnickel halides at 0°C, about ten moles per mole of the dimer were absorbed. The formation of a coordination bond corresponding to butenoylnickel dicarbonyl halides was observed by infrared spectroscopy:



$$\rightarrow 2CH_2=CHCH_2COX + 2Ni(CO)_4 .$$

In the presence of $Ni(CO)_4$, the carbonylation reaction is promoted by traces of acid (HCl), necessary for the formation of halogenonickel dicarbonyl hydride, which is apparently the actual reaction catalyst[133]:

$$HX + Ni(CO)_4 \underset{+2CO}{\overset{-2CO}{\rightleftharpoons}} HNi(CO)_2X \xrightarrow{RCH=CH_2} [RCH_2CH_2Ni(CO)_2X +$$
$$CH_3CH(R)Ni(CO)_2X] \xrightarrow{CO} [RCH_2CH_2CONi(CO)_2X + CH_3CH(R)CONi(CO)_2X] \rightarrow$$
$$\xrightarrow{R'OH} RCH_2CH_2COOR' + CH_3CH(R)COOR' + HNi(CO)_2X.$$

Data have been obtained in support of an analogous mechanism of the carbonylation reactions in the presence of a cobalt catalyst[134–137]. Acylcobalt carbonyl $RCOCo(CO)_4$, formed when the hydrocarbonyl $HCo(CO)_4$ absorbs a mole of carbon monoxide and a mole of olefin, was isolated. When $HCo(CO)_4$ was allowed to react with $RCOCo(CO)_4$, an aldehyde and $Co_2(CO)_8$ were obtained.

A mechanism has been proposed for the hydroformylation of olefins[134]:

$$RCH=CH_2 + HCo(CO)_4 \rightarrow RCH_2CH_2Co(CO)_4 \rightarrow RCH_2CH_2COCo(CO)_3 \rightarrow$$
$$\xrightarrow{CO} RCH_2CH_2COCo(CO)_4 \xrightarrow{HCo(CO)_4} RCH_2CH_2CHO + Co_2(CO)_8.$$

The reduction of $CH_3COCo(CO)_4$ by hydrogen at 25°C [138,139] ceases completely at high carbon monoxide pressures, which suggests that this acyl cobalt carbonyl is relatively inactive[139]. Therefore a different mechanism was adopted in which the catalyst is cobalt tricarbonyl hydride[136]:

$$HCo(CO)_4 \underset{+CO}{\overset{-CO}{\rightleftharpoons}} HCo(CO)_3 \underset{-RCH=CHR}{\overset{RCH=CHR}{\rightleftharpoons}} \underset{HCo(CO)_3}{RCH=CHR} \rightleftharpoons$$
$$\rightleftharpoons RCH_2CH(R)Co(CO)_3 \underset{-CO}{\overset{+CO}{\rightleftharpoons}} RCH_2CH(R)Co(CO)_4 \rightleftharpoons$$
$$\rightleftharpoons RCH_2CH(R)COCo(CO)_3 \begin{cases} \xrightarrow{HCo(CO)_4} RCH_2CH(R)CHO + Co_2(CO)_7 \\ \xrightarrow[H_2]{} RCH_2CH(R)CHO + HCo(CO)_3 \end{cases}.$$

Cobalt hydrocarbonyl catalyses also the migration of the double bond in olefins when it forms an intermediate π complex with the olefin[136,140].

The interconversion of alkylmetal carbonyl and acylmetal carbonyl takes place similarly also for the manganese compounds[141]. This is accompanied by the isomerisation of the carbon skeleton, for example:

$$CH_3CH_2CH_2CH_2COCo(CO)_n \rightleftharpoons \underset{H_3C}{\overset{H_5C_2}{\diagdown\!\diagup}}CHCOCo(CO)_n .$$

The rate of isomerisation greatly depends on the size of the alkyl group[142].

In the carbonylation and hydroformylation reactions, the true catalyst is probably cobalt hydrocarbonyl[137] which in the absence of gaseous hydrogen is formed from $Co_2(CO)_8$ and the hydrogen of the solvent. Acylcobalt carbonyls are hydrolysed or alchoholysed with formation of a carboxylic acid or an ester and the regeneration of the hydrocarbonyl. Acryloyl-, pent-4-enoyl, and allylcobalt tricarbonyls form with sodium methoxide the sodium salt of the corresponding acid, an ester, or an ether. Alkylcobalt and acylcobalt carbonyls form at 0°C stable complexes with $(C_6H_5)_3P$, carbon monoxide being evolved[135]. Trialkyl- and triaryl-phosphine derivatives $RCOCo(CO)_n$ react with sodium methoxide, forming free phosphines, $NaCo(CO)_n$, and carboxylic acid esters[137].

Iron carbonyls proved to be active catalysts in the carbonylation of olefins with formation of alcohols:

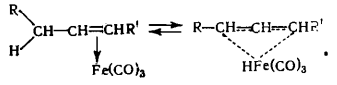
$$C_nH_{2n} + 3CO + 2H_2O \rightarrow C_{n+1}H_{2n+3}OH + 2CO_2 .$$

The reaction proceeds at 60–80°C and 100–200 atm in an aqueous alkaline solution of $Fe(CO)_5$. [143] The replacement of CO in the carbonyl by $(C_6H_5)_3P$ leads to an increase of catalytic activity by a factor of about ten[144]. The complexes formed from iron carbonyls, tertiary amines, and water are also active catalysts of this reaction[145], which occurs at a pressure as low as 10–25 atm. In the presence of ammonia, amines are formed[146].

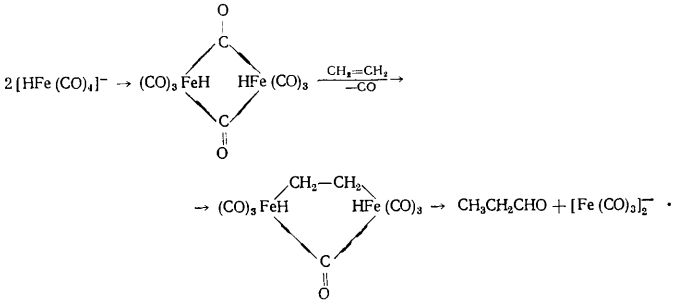
The synthesis of butyl alcohols by this method, has been achieved under industrial conditions[147]. Trimethyl-, and triethyl-amines and *N*-ethylpiperidine are most effective as the amine components of the catalyst. In this case the yield of alcohols reaches 56%. The effectiveness of pyridine and its derivatives is very low[148]. The complex of iron hydrocarbonyl with n-butylpyrrolidine also proved to be an active catalyst for the synthesis of primary butyl alcohols from propene. The conversion of carbon monoxide reached 75%, that of propene 86%, and the content of isobutyl alcohol was 25%.[149] The formation of some alcohols with the iso-structure indicates an isomerising effect of $Fe(CO)_5$.[145] The reaction probably proceeds via a π complex of iron hydrocarbonyl with the olefin in equilibrium with the σ compound[150]:

$$\underset{\downarrow}{RCH=CHR} \rightleftharpoons \underset{\downarrow}{RCH-CH_2R}$$
$$HFe(CO)_3 \qquad Fe(CO)_3$$

The formation of a π complex of the olefin with iron tricarbonyl, which is subsequently converted into a π-allyl complex of iron hydrocarbonyl, is also possible:



The complexes obtained by the reaction of $Fe(CO)_5$ with bases catalyse also the migration of the double bond in olefins. The olefin replaces one CO group and an aldehyde is obtained from the complex formed[151]:



In the carbonylation of olefins in the presence of ammonia or amines using cobalt catalysts at an elevated pressure, carboxylic acid amides are obtained. In the presence of iron catalysts, mainly primary, secondary, and ternary amines are formed, while the yield of the amides is low. The amides can be synthesised also on the catalyst for the Fischer–Tropsch synthesis (Co–ThO_2–MgO–kieselguhr) at 200°C and 150 atm. *N*-(n-propyl)propionamide, 2-ethyl-3,5-dimethylpyridine, and 4-ethyl-3,5-dimethylpyridine were synthesised from ethylene, ammonia, and a 1 : 1 carbon monoxide–hydrogen mixture in hexane. In the absence of hydrogen, *N*-(n-propyl)propionamide was obtained from ethylene, carbon monoxide, and n-propylamine in 60, 55, and 30% yields in the presence of the cobalt catalyst, Co + $Fe(CO)_5$, and $Fe(CO)_5$ respectively.

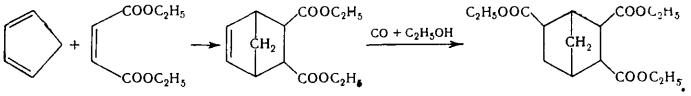
Unsubstituted cyclohexanecarboxamide was synthesised from cyclohexene, carbon monoxide, and ammonia. When ammonia was replaced by a primary amine, the reaction proceeded more smoothly; in the presence of hydrogen, amines are formed as side products[152].

The carbonyls $[C_6H_5Fe(CO)_2]_2$, $[C_6H_5Mo(CO)_3]_2$, and $[Co(CO)_4]_2$ catalyse the reaction of olefins, carbon monoxide, and carbon tetrachloride with formation of compounds having the general formulae RCH(COCl), CH_2CCl_3, and $RCHClCH_2CCl_3$.[153]

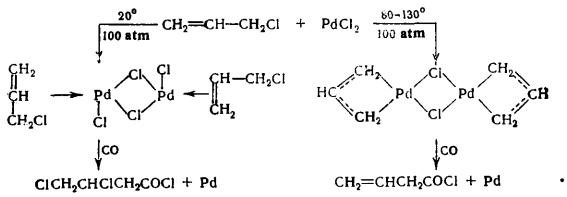
Group VIII noble metals, their salts, and complexes proved to be active catalysts for the carbonylation of olefins. Metallic palladium was active only in the presence of HCl. In the presence of "catalytic" amounts of these metal halides, carboxylic acid chlorides, anhydrides, and esters were formed from olefins, carbon monoxide, and hydrogen chloride in inert solvents at 150–200°C and 600–1000 atm.[154–157]. The reaction of carbon monoxide in benzene solution at 20°C and 50 atm with the Π complex

$C_2H_4.PdCl_2$, prepared by the reaction of ethylene with powdered $PdCl_2$ in benzene, gave β-chloropropionyl chloride in 40% yield relative to the initial *II* complex[155]. An ester of the β-chloroacid is formed in alcoholic solution. The corresponding esters of β-chloroacids were also obtained from C_3-C_5 olefins, carbon monoxide reacting with the terminal carbon atom of the double bond. However, hex-1-ene gave an ester with a branched structure as the main product. An ester of *trans*-2-chlorocyclohexanecarboxylic acid was obtained from cyclohexene. The yields of acid chlorides and esters are low due to the decomposition of a considerable proportion of the π complex with formation of an olefin or a chloro-derivative[158]. At 100 atm and 80°C, ethyl propionate with an admixture of ethyl β-hydroxypropionate and γ-oxocaproate was obtained from ethylene in ethanol saturated with hydrogen chloride in the presence of small amounts of $PdCl_2$, propene gave ethyl n-butyrate and isobutyrate (2:1), and styrene gave ethyl α- and β-phenylpropionates (2:1) with an admixture of α-chloroethylbenzene[155].

In the presence of the complex $[(C_6H_5)_3P]_2PdCl_2$, the carbonylation of olefins leads to the formation of carboxylic acids. In the presence of $[(C_6H_5)_3P]Pd$ and small amounts of hydrogen chloride at 90°C and 700 atm, about 60% of isobutyric acid, 3% of butyric acid, and 36% of methyl butyrate were obtained from propene, carbon monoxide, and methanol.[159] Products of the Diels–Alder synthesis, which are unstable at high temperatures, were carbonylated with the aid of palladium complexes:



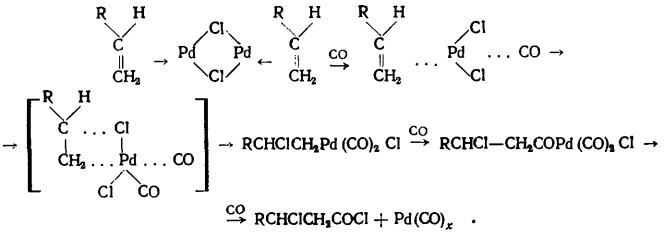
Triethyl cyclohexane-1,2,5-tricarboxylate was synthesised from butadiene by a similar reaction[160]. The differences sometimes observed in the mode of carbonylation depending on the reaction conditions, with formation of β-chlorocarboxylic acid chlorides or esters at 20°C and the analogous derivatives of β-unsaturated acids at 80–130°C, may be explained by the formation of different olefin–$PdCl_2$ π complexes,[158,161]:



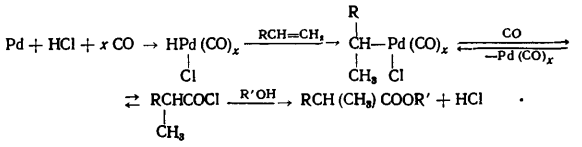
Carbonylation with retention of the double bond takes place with allyl chlorides and allyl alcohols, the same products being obtained from different isomers in consequence of the formation of the same π complex with $PdCl_2$.[159]

In the presence of Group VIII metal halides and chelate complexes in pyridine, olefins react with carbon monoxide and water, also with formation of ketones. Diethyl ketone was obtained from ethylene at 200°C and 1000 atm together with propionic acid, while propene gave acetone, isopropyl ketone, and isobutyrate together with isobutyric acid[162].

In the formation of acid chlorides and esters, the π complex of the olefin with $PdCl_2$ is coordinated to one or two carbon monoxide molecules; in the resulting complex the Cl atom migrates from palladium to the carbon atom of the coordinated olefin and a σ-organometallic compound is formed and reacts further with carbon monoxide. The latter is inserted between the alkyl group and palladium with formation of a β-chloroacylpalladium compound, which is subsequently converted into the chloride of the β-chlorocarboxylic acid:

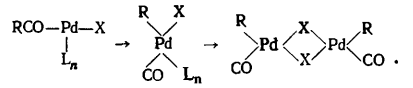


The structure of the initial π complex has been confirmed by NMR data[163]. A mechanism has been proposed for the formation of esters from olefins in the presence of the $PdCl_2$ in ethanol, where the true catalyst is palladium hydrocarbonyl chloride[164–168]:



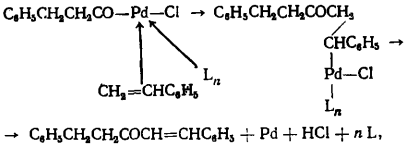
The $C_2H_4-PdCl_2$ complexes are carbonylated with formation of β-chloropropionic acid anhydride, while metallic palladium catalyses the carbonylation of olefins with formation of esters and aldehydes. These reactions are reversible: acid chlorides and aldehydes are decarbonylated to the olefins with intermediate formation of the acyl-palladium bond[165–167]. The first stage in the carbonylation of mono-olefins in the presence of hydrogen halides is believed to be the formation of palladium(II) in the form of metal hydride complexes, whose formation by oxidative addition of the hydrogen halide or hydrogen to transition metals is well known[169,170]. These complexes play an important role as catalysts, not only in carbonylation reactions but also in hydrogenation, double bond migration, and addition reactions.

A number of stages in carbonylation, catalysed by metal carbonyls, including the carbonylation of the phosphine complexes of palladium and platinum, are reversible[171]. The last decarbonylation stage—the conversion of the acylpalladium complex in the absence of carbon monoxide into an alkylpalladium complex proceeds via a "stable tetracoordinate bridge" halogenocarbonyl complex[172] [wrong reference (Ed. of Translation)]:



Subsequently the alkyl–palladium bond is cleaved with formation of an olefin and hydrogen halide or hydrogen. An alkyl palladium–phosphine complex with a β-hydrogen atom in the alkyl group is converted into an olefin and palladium hydride, which decomposes into palladium and hydrogen halide[173].

The decarbonylation of β-phenylpropionic acid anhydride gives 1,5-diphenylpent-1-en-3-one according to the mechanism[165]:



where L = phosphine.

The presence of activators (acids), the solvent, and reaction temperature have a major influence on the redistribution of bonds within the palladium complexes on coordination of carbon monoxide and the dissociation of Pd–Cl bridge bonds[174].

The decarbonylation of carboxylic acid chlorides also takes place under the influence of rhodium complexes:

$$RCH_2CH_2COCl + RhCl[(C_6H_5)_3P]_3 \rightarrow RCH{=}CH_2 + HCl + Cl{-}Rh(CO)[(C_6H_5)_3P]_2 .$$

The chlorocarbonyl complex formed could be isolated[165].

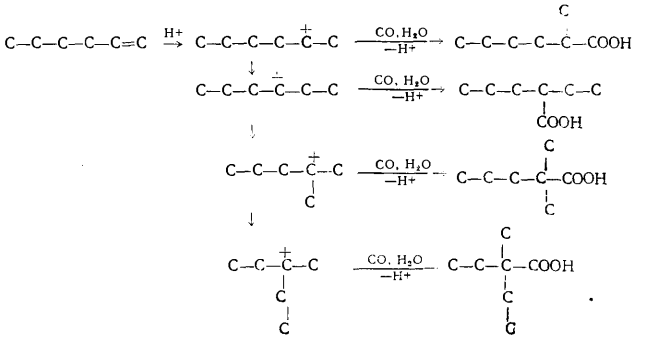
The decarbonylation of aldehydes leads to the formation of an alkane and the complex $ClRh(CO)[(C_6H_5)_3P]_2$.[166] This complex was also obtained by the reaction of the transition metal salts with alcohols, and proved to be an active catalyst for the decarbonylation of aldehydes and acid chlorides[175,176]. Analogous carbonyl halide hydrides are formed by the reaction of hydrogen chloride with carbonylbis(triphenylphosphine)iridium chloride[170] and of methyl chloride with iodo(methyl)bis(triethylphosphine)-platinum[177]. In the presence of soluble variable-valence metal salts, with a positive oxidation potential higher than that of platinum, for example $CuCl_2$, platinum catalyses at 120–150°C and 150–200 atm the carbonylation of olefins in an alcoholic medium with formation of unsaturated and β-alkoxy-substituted carboxylic acid esters. Oxygen was added in portions to the reaction medium[178]. αβ-Unsaturated carboxylic acid esters have been synthesised electrochemically[178,179] from carbon monoxide and olefins in the presence of carbonyl complexes of platinum. It has been suggested that the catalytic activity of Group VIII metal carbonyls in the carbonylation of unsaturated hydrocarbons is associated with the acidic properties of the hydrocarbonyls of these metals, rhodium carbonyl showing the greatest effectiveness in the hydrocarboxylation and hydromethoxycarbonylation reactions of the above hydrocarbons[180].

Ruthenium and rhodium halides and chelate complexes also catalyse the carbonylation of olefins. Propionic acid is formed from ethylene in concentrated hydrochloric acid and in cyclohexane solution mixed with anhydrous hydrogen chloride the products are propionic anhydride and propionyl chloride. The reaction proceeds at 150–210°C and a high carbon monoxide pressure (600–1000 atm).[154]

The data quoted in this section show that the carbonylation of mono-olefins with formation of saturated carboxylic acids in an aqueous medium or of their esters in an alcoholic medium proceeds in the presence of catalysts based on Group VIII metals; cobalt, nickel, iron, platinum, palladium, ruthenium, and rhodium. The true catalysts are the intermediate hydrocarbonyl complexes. One of the primary stages may be the formation of a π complex of the metal hydrocarbonyl with the olefin. An important stage is the conversion of the alkyl into acyl complexes. Catalysts based on Group VIII noble metals, particularly complexes with ligands of the type of triarylphosphines, are already active at 20–50°C and the reaction products can be also acid chlorides, anhydrides, and chlorocarboxylic acids.

2. Reactions in the Presence of Acid Catalysts

The carbonylation of olefins can be achieved in the presence of various acid catalysts[1]. Initially the reaction was carried out at an elevated temperature (100–300°C) and high carbon monoxide pressures (200–1000 atm) in the presence of all the starting materials in the reaction zone. Subsequently the process was achieved in two stages: the reaction of the olefin with carbon monoxide in the presence of 96% sulphuric acid at 0–50°C, and 1–100 atm carbon monoxide pressure and the decomposition of the reaction complex by water with formation of carboxylic acids and regeneration of sulphuric acid[181,182]. The addition of the elements of formic acid (H–COOH) takes place in accordance with the Markovnikov rule. Acids with a quaternary atom, such as αα-dimethyl- and α-ethyl-α-methylalkanoic acids, are always formed from straight-chain α-olefins together with the expected acids having a tertiary carbon atom in the α-position; unbranched carboxylic acids are absent from the reaction products. The number of possible isomers is given by the equation $y = x - 2$, where x is the number of carbon atoms in the initial olefin. All the expected isomeric acids were obtained from straight-chain C_5–C_{10} olefins[183]. The results obtained are described satisfactorily by a mechanism according to which carbonium ions are formed as intermediates:



Olefins branched at the double bond can form only tertiary carbonium ions and the latter are converted exclusively into carboxylic acids with a quaternary α-carbon atom.

Small amounts of the carbonylation products of the dimeric form of the olefin are formed together with the normal reaction products. Trimethylacetic[181,184] and ααγγ-tetramethylvaleric acid were obtained from isobutene. Lower olefins branched at the double bond disproportionate at a carbon atom with subsequent carbonylation. Thus a mixture of C_{11} acids and also equivalent amounts of trimethylacetic and αα-dimethylvaleric acid are formed from 2-methylbut-2-ene together with αα-dimethylbutyric acid. The formation of C_5 and C_7 acids is due to the disproportionation of the isodecene formed initially into C_4 and C_6 olefins. ααγγ-Tetramethylvaleric and methylneopentylacetic acids were obtained from di- and triisobutenes respectively.

For cyclic mono-olefins, the number of possible isomeric acids cannot be determined from the equation derived for unbranched acyclic olefins, since the isomerisation is affected by the ring size and ring strain and also the reaction conditions. 1-Methylcycloheptane- and 1-ethylcycloheptane-carboxylic acids were obtained from cyclo-octene; the products of the direct carbonylation of cyclononene and cyclodecene could not be obtained either[185].

When carbon monoxide is replaced by formic acid, the reaction in the presence of concentrated sulphuric acid proceeds at atmospheric pressure and room temperature[186–188]. Carboxylic acids are obtained in high yields for the molar ratios olefin: $HCOOH : H_2SO_4 = 1 : 4 : 8$. Carboxylic acids with one carbon atom more than in the initial olefin and with a quaternary carbon atom in the α-position were largely formed from unbranched olefins.

A mixture of the carbonylation products of the monomeric and dimeric forms and of the olefins produced by the disproportionation of the dimer was obtained from the olefins branched at the double bond. Cyclo-olefins without a six-membered ring usually undergo ring contraction or expansion with formation of cyclohexanecarboxylic acids. Cyclohexene gives 1-methylcyclopentanecarboxylic acid and alkylcyclohexenes are converted into acids with retention of the six-membered ring. Bi- and poly-cyclic systems are carbonylated in high yields (up to 95%). Thus 5-methyl-bicyclo[2,2,1]hept-2-ene gives 2-*endo*-methylbicyclo[2,2,1]heptano-*exo*-2-carboxylic acid[186].

In the synthesis of carboxylic acid esters using carbon monoxide, a two-stage method is employed, in which the reaction complex formed by the interaction of the olefin with carbon monoxide at 20–40°C and 70–80 atm carbon monoxide pressure in the presence of sulphuric acid is decomposed by methanol or ethanol[189-191]. C_5-C_{10} olefins[192-195] and cyclo-olefins[196,197] have been hydroalkoxycarbonylated by this method. Methyl and ethyl esters, predominantly with a quaternary α-carbon atom, are obtained in high yields[198]. At atmospheric pressure the yield of esters is low, but, on raising the carbon monoxide pressure in the range 5–75 atm, the overall yield of esters increases; however, in the case of isobutene the content of esters with quaternary and tertiary α-carbon atoms shows little change. In the reactions of straight-chain α-olefins, skeletal isomerisation processes are retarded, which leads to a lowering of the yield of esters with a quaternary α-carbon atom[199,200]. An increase of the H_2SO_4 : olefin molar ratio increases the overall yield and the content of the main reaction product for but-1-ene but decreases the content of the main product for isobutene. An increase of reaction temperature has an unfavourable effect[201].

The hydroalkoxycarbonylation of olefins and cyclo-olefins is readily achieved by the reaction with formic acid in the presence of concentrated sulphuric acid at atmospheric pressure close to room temperature with subsequent addition of the alcohol in the second stage of the process. The reaction has been investigated for aliphatic straight-chain C_5-C_9 olefins, C_5-C_6 olefins with the iso-structure[202-205], and also cyclo-olefins: cyclopentene, cyclohexene, 1-alkylcyclopentenes, and 1-alkylcyclohexenes[205-208]. C_1-C_5 saturated alcohols were used in the second stage. In all these reactions the main products were carboxylic acid esters with quaternary or tertiary carbon atoms in the α-position relative to the alkoxycarbonyl group. The corresponding free carboxylic acids were present in the reaction products. The position of the double bond in the initial olefin molecule did not affect the course of the reaction. The relative yield of esters fell and that of free acids increased with increase in the number of carbon atoms in the molecule of the alcohol added in the second stage[209-211].

An increase of the concentration of sulphuric acid, the addition to it of some P_2O_5, an increase of the relative amount of the alcohol added in the second stage, and in increase of temperature lead to an increase of the yield of esters. Thus in the case of pent-1-ene an 80% yield is achieved and the content of the main products in the mixture is 90–98%.

The isomerisation of the carbon skeleton of the initial olefin takes place in the alkylcarbonium ion stage and the acylium ion formed subsequently by the reaction $R^+ + CO \rightarrow R\overset{+}{C}O$, the carboxylic acid, and its ester do not isomerise. A certain amount of carboxylic acids is produced already in the first reaction stage due to the water contained in the sulphuric and formic acids and liberated on decomposition of the latter. Esters are formed both by the reaction of acylium ions with alcohols:

$$R\overset{+}{C}O + R'OH \rightarrow RCOOR' + H^+$$

and by the esterification of the carboxylic acids already formed in the first stage[212-214].

It has been noted[215] that concentrated H_3PO_4 does not catalyse the carbonylation of olefins at all. However, this proved true only of the reaction conditions described: 5–10°C and 100 atm carbon monoxide pressure. Subsequently it was found that at a higher temperature phosphoric acid is active in this reaction[216]. In the presence of 95–100% H_3PO_4, $H_4P_2O_7$, and polyphosphoric acids, C_5-C_{12} olefins of different structures were converted into carboxylic acids at 75–150°C. Under the reaction conditions, H_3PO_4 gives up the water necessary for the formation of a carboxylic acid, and is converted into $H_4P_2O_7$. When a stoichiometric amount of water is added, the catalyst and the reaction product collect in different layers[217]. The catalytic properties of H_3PO_4 were investigated in reactions involving the carbonylation by carbon monoxide of straight-chain C_5-C_{10} olefins, isobutene, di-isobutene, and cyclohexene[218-222]. A mixture of $\alpha\alpha$-dimethyl-, α-ethyl-α-methyl-, α-ethyl-, and α-methyl-alkanoic acids is formed as the main products.

Straight-chain C_7-C_{10} α-olefins yielded only acids derived from their monomeric form, i.e. with the C_8-C_{11} composition. C_5-C_6 α-olefins form in addition small amounts of acids derived from their dimeric form ($C_{11}-C_{13}$ acids), disproportionation products, and also the isomers and dimers of the initial olefin. Isobutene and di-isobutene give rise to the same reaction products: trimethylacetic acid and C_6-C_8 and C_{13} acids. 1-Methylcyclopentanecarboxylic acid, cyclohexanecarboxylic acid, and a mixture of *cis*- and *trans*-decalin-9-carboxylic acid were obtained from cyclohexene. The optimum concentration of H_3PO_4 in the carbonylation of C_7-C_{10} α-olefins increases with the number of carbon atoms in the olefin molecule; in the case of C_5-C_6 olefins, this concentration is below 94%. At higher concentrations the olefin dimerisation and disproportionation processes become intensified. With the increase in the number of carbon atoms in the molecule of the initial olefin from four to seven, the overall yield of acids rises with a relative decrease of the yield of acids having a quaternary carbon atom in the α-position and also derivatives of the dimeric form of the olefin. The optimum reaction temperature is in the range 125–175°C, i.e. higher by about 100°C than in the carbonylation in the presence of sulphuric acid. The optimum carbon monoxide pressure is 70–80 atm, which is higher by 20–30 atm than for sulphuric acid[220].

"Solid" phosphoric acid, prepared by mixing 90% phosphoric acid with kieselguhr and subsequent heat treatment at 200–370°C,[223] catalyses the carbonylation reaction at 50–100°C and 150 atm.

Hydrogen fluoride has also been used as a catalyst for the carbonylation of olefins. Carboxylic acid fluorides are formed from unbranched olefins and carbon monoxide in the presence of anhydrous HF, while in the presence of aqueous hydrofluoric acid the products are carboxylic acids and their esters. When methanol is added, esters are produced. α-Methylbutyric and isononanoic acids and their s-butyl esters were synthesised from but-1-ene at 30°C and a carbon monoxide pressure of 20–30 atm in the presence of HF containing 5% of water. Olefins branched at the double bond are carbonylated more readily than straight-chain olefins, but the reaction products are

carboxylic acid and their fluorides. Esters are not obtained under these conditions because of the instability of the intermediate tertiary alcohols, which are decomposed by hydrogen fluoride. Esters are obtained from C_3-C_{20} olefins and carbon monoxide at higher pressures in the presence of hydrogen fluoride and up to 15% of water. When the initial compounds are measured out accurately, hydrogen fluoride can be reused without additional purification [224-227].

Catalysts based on BF_3, which can be separated from the reaction products without diluting the reaction mixture with water or alcohols, are also employed in the olefin carbonylation reactions. The $BF_3-H_2SO_4$ systems, prepared by passing BF_3 into 45 and 85% sulphuric acid at 0° and 100°C, are used only for branched olefins [215,228,229] and the $BF_3-H_3PO_4$ system, with component ratios ranging from 1.2 : 0.8 to 0.8 : 1.2, is used for the carbonylation of both branched and unbranched olefins. The greater the amount of carboxylic acids with a quaternary α- carbon atom in the reaction products, the more complete and rapid is their separation from the catalyst [230-232].

The BF_3-CH_3OH system, obtained by passing BF_3 into methanol, may be regarded as monomethoxyfluoroboric acid $H(BF_3OCH_3)$; it is active in the hydroalkoxycarbonylation of olefins, particularly cyclic olefins, but it results in a homogeneous reaction mixture [233], which does not separate into the catalyst and the reaction product. In the presence of this system at 15°C and a carbon monoxide pressure of 150 atm, high yields were obtained of the methyl esters of 1-benzylcyclohexanecarboxylic, 1-benzylcycloheptanecarboxylic, and 1-benzylcyclooctanecarboxylic acids from 1-benzylcyclohexene, 1-benzylcycloheptene, and 1-benzylcyclo-octene respectively [234], the methyl esters of C_{12} and C_{23} acids from undec-1-ene, and also the corresponding esters of acids derived from oct-1-ene, isononene, isobutene, tetradec-1-ene, 2-ethylhex-1-ene, and octahydronaphthalene. A mixture of alkoxyfluoroboric acid with boron trifluoride hydrate, containing between one and two moles of a mixture of water and alcohol per mole of BF_3, also catalyses effectively the carbonylation of olefins. When a stoichiometric amount of water is added, the catalyst is readily separated from the reaction products, which consist of a mixture of 70-90% of carboxylic acids and 3-20% of their esters [235].

The BF_3-2H_2O system, obtained when BF_3 is passed into water at 0°C, is active in the carbonylation of olefins. Branched olefins are converted below 10°C and at 50-100 atm into acids in 85% yield. In the presence of $BF_3 . 1.5H_2O$, the trimer of propene reacts at 20°C, giving a high yield of a mixture of not less than eight isomeric C_{10} acids [215,236]. The optimum yield of trimethylacetic acid is obtained from isobutene at a carbon monoxide pressure of 100 atm, 30°C, and the molar ratio $C_4H_8 : BF_3 . 2H_2O = 1 : 1$. [237]

The data presented in this section show that two-stage olefin hydrocarboxylation and hydroalkoxycarbonylation reactions involving carbon monoxide, a compound with a mobile hydrogen atom, and an acid catalyst permit the synthesis of branched carboxylic acids with tertiary and quaternary carbon atoms in the α-position, their esters, and certain derivatives.

The acid catalysts are concentrated sulphuric acid, concentrated phosphoric acid, hydrogen fluoride, and boron trifluoride complexes.

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Mixtures of Aminoacids in Human Nutrition

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The use of mixtures of individual aminoacids instead of proteins in human nutrition has been the subject of numerous recent investigations. The aim was not only to investigate the process of aminoacid assimilation itself but also to elucidate the question of their possible long term use in food. The large scale and prolonged employment of aminoacid mixtures in therapeutic feeding shows that they constitute an adequate replacement of food proteins and their consumption does not apparently entail any undesirable consequences. Various aspects of the use of aminoacids to improve the nutritional value of second-class proteins by adjusting their [aminoacid] balance are also discussed. However, before reaching final conclusions concerning the ways of utilising aminoacids in nutrition, more prolonged and comprehensive studies are necessary. The review deals with work carried out in the last 10 years.
The bibliography includes 164 references.

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I. INTRODUCTION

A considerable proportion of the earth's population, particularly in certain countries in Asia, Africa, and Latin America, suffers nowadays from a chronic deficiency of foodstuffs, mainly protein, which leads to high child mortality both from the malnutrition itself and from the reduced resistance of the organism to infectious diseases and possible genetic damage caused by malnutrition. Owing to the high rate of increase of the populations of these countries, the situation is continually deteriorating[1].

The intensification of agriculture, the use of protein products previously not employed in food, and the tapping of the resources in the ocean are the most obvious ways of solving this problem. These ways are based on an extensive agriculture, i.e. harvesting the crop from larger areas. In addition they inevitably interfere with the earth's ecological system[2].

A new and promising method of obtaining foodstuffs is chemical synthesis. Where protein is concerned, this involves the synthesis of aminoacids and their mixtures and if necessary of polymers from inorganic non-food raw materials[3,4]. Apart from other considerations, this procedure has the advantage that it gives a high yield of production per unit productive area.

However, in an examination of the possible utilisation in food of such products, a number of problems concerning the physiology and biochemistry of nutrition arise. Naturally, before introducing into human nutrition any kind of synthetic diet, one must develop compositions of the latter such that the normal functioning of the human organism, accustomed throughout evolution to food of plant and animal origin, is ensured. This is an exceptionally complex problem.

Body-tissue material and energy are introduced into the organism with food. Although the adaptive capacity of the organism to various sources of food is high, it is nevertheless limited. Therefore excessive abuse of this capacity can eventually lead to the breakdown of the functions of the regulating mechanisms in digestion, which is revealed in a wide variety of diseases associated with different types of food deficiency and when the proper proportions of the nutrient substances in the diet are not maintained. Owing to its internal reserves, the organism itself can correct many errors in the rations, but it does appear to be more satisfactory to extend our knowledge in the field of nutrition in order to provide the organism with its essential requirements to the maximum possible extent. The nature of food to some extent induces the secretion of digestive enzymes—their activity and amount.

The requirement for essential individual food components, including aminoacids, is due to the fact that the organism lacks enzyme systems which can synthesise them at a sufficient rate from non-specific metabolic intermediates. Therefore a thorough investigation of the effect of essential nutrient factors as such on the organism as a whole is necessary before they are introduced into human diet.

The aim of the present review is to examine work concerning the use of synthetic or more precisely monomolecular nutrient substances, primarily aminoacids, in human nutrition.

II. NITROGEN BALANCE AND BIOLOGICAL VALUE OF PROTEINS, AMINOACIDS, AND THEIR MIXTURES

On entering the human organism, protein is fully hydrolysed in the digestive tract to aminoacids, which pass into the blood only in this form and are supplied to all the tissues and body organs where protein is resynthesised. There are data showing that proteins introduced parenterally also break down into aminoacids before being utilised by the organism[5].

Table 1. Soluble diets for the feeding of human patients *per os*.

Substance	Diet according to Winitz*	Diet of Schwartz Bioresearch Inc.
Carbohydrates	(g)	(g litre^{-1})
Glucose	550.0	418.1
Glucono-δ-lactone	17.2	–
Gluconoaldehyde	–	12.8
Aminoacids		
Lysine.HCl	3.58	2.64
Leucine	2.83	2.82
Isoleucine	2.42	1.78
Valine	2.67	1.96
Phenylalanine	1.75	1.29
Methionine	1.75	1.29
Threonine	2.42	1.78
Tryptophan	0.75	0.55
Alanine	2.58	1.90
Arginine.HCl	2.58	1.90
Histidine.HCl.H_2O	1.58	1.16
Glycine	1.67	1.23
Glutamine	9.07	5.0
Na aspartate	6.40	4.05
Na glutamate	–	3.83
Proline	10.33	7.58
Serine	5.33	3.92
Tyrosine ethyl ester.HCl	6.83	5.03
Cysteine ethyl ester.HCl	0.92	–
Water-soluble vitamins	(mg)	(mg litre^{-1})
Ascorbic acid	62.50	46.0
(+)-Biotin	0.83	0.58
B_{12}	1.67	1.25
Inositol	0.83	0.59
(+)-Aminobenzoic acid	416.56	307.1
Thiamin.HCl	1.00	0.74
Nicotinamide	10.00	7.36
Pyridoxine.HCl	1.67	1.25
Ca (+)-pantothenate	8.33	6.11
Folic acid	1.67	1.25
Choline hydrogen tartrate	213.25	–
Choline chloride	–	92
Riboflavin	1.50	1.10
Fat-soluble vitamins	(mg)	(mg litre^{-1})
Vitamin A acetate	3.64	5.0
Vitamin D	0.057	–
α-Tocopheryl acetate	57.29	25.0
Calciferol 40 ME/MG	–	3.5
Menadione	4.58	2.1
Polysorbate 80	–	3.0
Ethyl linoleate	200	260
Salts and microelements	(mg)	(mg litre^{-1})
Manganese acetate.$4H_2O$	18.30	13.48
Copper acetate.H_2O	2.50	1.84
Cobalt acetate.$4H_2O$	1.67	1.23
Ammonium molybdate.$4H_2O$	0.42	0.31
Zinc benzoate	2.82	1.49
Zinc acetate	–	1.49
Potassium iodide	0.25	0.18
	(g)	
Potassium hydroxide	3.97	–
Magnesium oxide	0.38	–
Sodium chloride	4.77	–
Na glycerophosphate	5.23	–
Iron(II) gluconate	0.83	–
$CaCl_2.2H_2O$	2.44	–
Sodium benzoate	1.00	–

* All the dry substances were dissolved in distilled water to give a concentration of 50–70%.

Therefore many investigators decided to test directly the effect of introducing into the organism various amino-acid compositions instead of proteins. In experiments on rats, Greenstein et al.[6] showed that diets comprising chemically pure monomers can support growth, reproduction, and life of the experimental animals throughout several generations. Subsequently Winitz et al.[7] demonstrated the possibility of using such diets also to support normal life in healthy man. During a 19-week experimental period 24 male volunteers aged between 24 and 39 were kept on a synthetic diet, whose composition is presented in Table 1.

Physiological observations showed that they all became accustomed to such diets; throughout the experimental period, a positive nitrogen balance was maintained in the majority of the individuals tested.

It is believed that the subject is in nitrogen balance when the amount of nitrogen received with food (I) is equal to the amount eliminated from the organism in urine (U), faeces (F) and via the skin (S):

$$I = U + F + S\,.$$

If I exceeds the sum $U + F + S$, a positive nitrogen balance is obtained, otherwise the balance is negative.

Thus the nitrogen balance is the fundamental criterion in the estimation of the protein state of the organism. If the organism is maintained for a long time in a negative nitrogen balance, its protein reserves are exhausted with an eventual lethal outcome.

In order to maintain a nitrogen equilibrium, different amounts of different proteins are required. If the amount of a protein required to maintain equilibrium is small, the protein is said to have a high biological value. In general the nutrient value of protein is determined by two different factors: (1) digestibility and (2) biological value[8].

Digestibility is determined by the ratio of the absorbed protein elements to the amount introduced. It depends on the exocellular and endocellular proteolythic activity of the intestine and the capacity of all the intestines for absorption. Digestibility is related to the necessity for the simultaneous introduction of all essential aminoacids into the reaction medium during synthesis. The biological value (BV) indicates the ratio of the protein elements absorbed and retained by the organism.

According to the classification adopted by FAO/WHO [9],

$$\mathrm{BV} = \frac{\text{retained nitrogen}}{\text{absorbed nitrogen}}$$

The biological value depends both on the aminoacid composition of the protein and on the digestion and transport of the nutrient substances. In terms of nutrient value, the proteins of mother's milk (90–97%), eggs, cow's milk, cheese, meat, fish (80–90%), and yeast (77%) come first, are followed by grain proteins, and finally by wheat flour (54%).

The studies on the effects of individual aminoacids in proteins on the biological value of the latter begun as early as the beginning of the 20th century by Kellner, Willsk [Wills ?], Hopkins, Abderhalden, Osborn, Mendel, and others, were completed by the systematic work of Rose, who, as it were, summed up the studies concerning the elucidation of the role of protein in nutrition. The nutritive value of protein is closely related to its composition, namely to the content and relative proportions of essential aminoacids. Rose was the first investigator who studied systematically the effect of individual amino-acids on the nitrogen balance. The nitrogen balance technique, which he was the first to employ, still remains the foundation of all metabolic experiments involving human nutrition by aminoacid mixtures[10].

Hegsted[11] quotes different versions of the human requirement for aminoacids (Table 2).

The norms in aminoacid requirement were proposed by the FAO committee in 1957 and were then revised by FAO/WHO experts in 1965.[9] The same organisations put forward as a criterion of protein nutrition the ratio of essential aminoacids (E) to the total amount of nitrogen in a particular protein (T). The E/T ratio is expressed in milligrammes of essential aminoacids per gramme of total nitrogen. Proteins with high, medium, and low nutrient values have E/T = 3, 2, and below 2.

Table 2. Average aminoacid requirements of adult humans.

Aminoacid	For women (according to D.M.Hegsted)		Published data (according to W.C.Rose)		
	mg/day		for women	for men	
			mg/day		
	amount of amino-acids required to maintain a zero nitrogen balance	amount of amino-acids required to maintain an amino-acid balance of +0.5 g/day		minimum	optimum
Tryptophan	168	270	157	250	1200
Phenylalanine in the presence of tyrosine	258	550	220	300	—
Threonine	375	1750	305	500	3600
Isoleucine	550	1700	450	700	3000
Lysine	545	1750	500	800	6000
Methionine (+ 500 mg of cystine)	194	375	180	200	—
Methionine (+ 10 ml of cystine)	700	3450	550	1100	—
Valine	622	1000	650	800	4200
Leucine	727	2600	620	1100	5400

According to Rose, the requirement for protein reduces to 2 sources of nitrogen: (1) essential aminoacids which the organisms cannot synthesise and (2) non-specific additional nitrogen for the synthesis of other aminoacids and nitrogen-containing compounds. The latter can consist either of a single aminoacid or a mixture of non-essential and essential aminoacids. It can be provided also in another form, for example in the form of urea, diammonium citrate, etc. Thus animal and human organisms require both essential and non-essential nitrogen.

Comparing the biological value of natural proteins and the equivalent aminoacid mixtures imitating their compositions both qualitatively and quantitatively, some investigators suggested that the effectiveness of such mixtures is lower than that of protein[12-21]. This conclusion was made largely on the basis of the decrease of the nitrogen balance, loss of appetite, the shortening of the feeding period, and the arrest of growth in young animals. There arises the valid question to what extent one can rely on conclusions based on experiments on laboratory animals with the aim of transferring them to human beings.

In an early paper Hegsted[22] noted that there is a close relation between the aminoacid requirements of man and animals, since the differences in their body structures are not all that great. The rat, being a more rapidly growing animal than man, has a higher overall requirement for nutrient substances. Moreover, the rat's requirement for methionine is higher, due to the growth of its hair covering. It also has a higher requirement for lysine (lysine is known to be required more for growth than for the maintenance of the nitrogen balance). However, the assertion that aminoacid mixtures tested on animals are less effective cannot be regarded as fully reliable, since there are many studies with the opposite findings[23-32].

Guggenheim and Szmelcman[33] actually demonstrated a higher effectiveness of the mixture compared with protein. When rats were maintained on a diet consisting solely of an aminoacid mixture, they gained more in weight and had a higher protein content in their serum and also more nitrogen in RNA and in the liver than the animals receiving the same amount of protein as casein. Sauberlich[32] suggests that correctly balanced aminoacid mixtures can fully replace proteins in diet without an arrest of growth.

III. CAUSES RESPONSIBLE FOR DIFFERENT MODES OF UTILISATION OF PROTEINS AND AMINOACID MIXTURES

These conflicting data led to a number of hypotheses explaining the possible cause of the different ways of utilisation of proteins and aminoacid mixtures. Thus it has been suggested that the rates of absorption of monomeric and polymeric substances are different. Rose and Clark believe that monomers are absorbed faster. However, the studies in recent years showed that the hydrolysis products of food proteins are absorbed at the same rate as the equivalent monomer solutions[34]. Absorption then takes place at an equal and constant rate, is rigorously coordinated, and is of a competitive type[35].

The idea of the possible utilisation of the aminoacids from mixtures by the bacterial flora of the intestine has also been put forward. Abderhalden suggested that the period during which aminoacids derived from proteins remain in the intestine is much shorter than when the free mixtures are introduced. Therefore they are "captured" by bacteria and are at the same time converted into toxic substances. Abderhalden failed to take into account the fact that the diameter of the pores in the filaments of the so called "brush border" of intestinal epithelium, where the concluding stage of the formation of free aminoacids and hexoses takes place, is too small (of the order of 100–200 Å) to allow penetration by bacteria. Therefore aminoacids from proteins cannot be available to bacteria. However, when a complete mixture of monomers is provided, they must be inevitably supplied to bacteria. This view is supported by Ugolev[36]. The reason for undesirable effects in this case may be the multiplication of bacteria, the entry of ammonia and toxic amines into the bloodstream, and the breakdown of dietary balance. Fears were voiced that the gastric intestinal tract may degenerate owing to the reduced functional requirements.

Another consequence of the low molecular weight of the aminoacid may be the so called "osmotic effects" expressed in digestive disorders, vomiting, diarrhoea, etc.[37,38]

Shishova-Kasatochkina et al.[21] suggest that the growth factors, vitamin B_{12}, vitamin A_1, streptogenins, etc. contained in natural proteins, ensure a higher nutrient effectiveness of protein. Moreover, it may be that certain protein-like bonds, providing the synthetic processes in the organisms with additional energy evolved on their dissociation, are absent from the mixtures. This results in a higher calorie requirement in the aminoacid diet compared with the protein diet. In the same study the authors demonstrated on sterile animals that the intestinal microflora does not constitute an obstacle to the utilisation of aminoacid mixtures.

Other workers[39] believe that protein may have an effect on the production of enzymes in the small intestine

and also may act as an agent preventing the inactivation of these enzymes.

A number of investigators relate the effectiveness of the utilisation of mixtures to the intake of the total energy, total nitrogen, and its quality. It was established long ago that, when an aminoacid mixture is ingested by man, it is necessary to introduce more energy into the organism than in the ingestion of casein[40]. In later studies on rats this observation was not confirmed[41]. However, six years later, Akrens et al.[39] undertook a study of the same effect. They carried out a comparative feeding of two groups of rats of different ages with casein and an aminoacid mixture imitating it. For both old and young animals, there was no difference in the gain of weight as a function of the source of nitrogen (from the protein or from the aminoacid mixture) at a low-calorie level of intake. On the other hand, when the rats received a high-calorie diet, the gain in weight was greater with the casein feed.

Kies and Linkswiler[42] showed on man a significant relation between the requirement for a specific amount of essential aminoacids and the level of calorie intake. Thus with increase of the daily intake from 35 to 55 kcal per kilogramme body weight, the fraction of 8 essential aminoacids required to maintain a positive nitrogen balance was reduced.

Swendseid[43] examined the problem of the effect of the total amount of dietary nitrogen on the requirement for essential aminoacids. A number of studies on 60-year-old men showed that their aminoacid requirement increased with the amount of nitrogen in the diet. On the other hand, this type of relation was not observed in experiments on young men and girls. Swendseid notes that this problem is of interest in connection with the establishment of a relation between the total nitrogen, essential aminoacids, and the requirements for them associated with age.

Young and Zamora[44] showed that the level of nitrogen in the diet has little effect on growth when the intake of essential aminoacids is low; for relatively high intakes, in excess of 10% of the total diet, growth is better maintained for higher total nitrogen levels in the diet. The positive results of the introduction into the aminoacid mixtures of an additional amount of arginine, which reduces the toxicity of the ammonia produced on feeding aminoacid mixtures, were noted. Ranhotra and Johnson[30] found that, when newly born rats are fed with a pure aminoacid mixture equivalent to protein, an approximately similar gain in weight is achieved as on feeding with a protein diet. This gain was obtained as a result of an increase in the amount of dietary arginine compared with that employed previously. The optimum requirement for arginine hydrochloride is apparently 0.5% of the total weight of the diet.

Hepburn and Bradley[31] emphasised the protective role of glutamine in aminoacid diets. It also has a detoxicating effect.

The best effect as regards the increase in weight of growing animals was produced by the following mixture of essential aminoacids (expressed in percentages of the dry rations, all in the L-form): histidine 0.25, lysine 0.90, tryptophan 0.11, isoleucine 0.55, valine 0.55, leucine 0.70, threonine 0.50, methionine 0.16, cystine 0.34, phenylalanine 0.42, and tyrosine 0.30.[45]

Despite the proven suitability of aminoacid mixtures in the feeding of experimental animals, the compositions tested directly on human beings are nevertheless of particular interest.

Examination of the literature shows that, in all cases where the suitability of aminoacid mixtures in nutrition was investigated by direct experiments, there was no doubt about the equivalence of aminoacids mixtures and protein.

IV. DETERMINATION OF THE REQUIREMENTS OF THE ORGANISM FOR AMINOACIDS

As already mentioned above, the principal technique adopted to discover the requirement for a particular aminoacid is the nitrogen balance method. In addition, many investigators, in particular Almquist, believe that there is a close relation between the plasma aminoacids and the protein level in the diet. This might in turn serve as a direct method for the determination of the aminoacid requirement.

Exact methods for the quantitative determination of aminoacids (ion-exchange and gas chromatography, sensitive aminoacid analysers, etc.) make it possible to compare the aminoacid composition of the plasma with that of the aminoacid mixtures or protein employed. Morrison et al.[46] established a relation between lysine-deficient diets and the level of lysine in the plasma. Analogous investigations of the plasma and dietary levels of lysine, arginine, and valine were reported by Zimmerman and Scott[47].

McLaughlan and coworkers[48-53] have been concerned with the same problem for many years. They demonstrated an almost linear relation between the amount of free plasma aminoacids and their level in the diet. The same investigators concluded that the method used to detect plasma aminoacids can be applied to determine the human aminoacid requirement.

However, later the same workers[54] established that the method used to determine the blood aminoacids is suitable for the determination of the limiting aminoacids in the diet only when there is a deficiency of one or two limiting aminoacids but is virtually unsuitable for the prediction of a multiple aminoacid deficiency in the diet.

Interesting data in this respect were presented by Swendseid in her report delivered in the summer of 1968 in the Institute of Organic Derivatives of the Elements of the USSR Academy of Sciences. The experiments were performed both on young people—college students (men and women)—and middle-aged people. Measurements were made of the plasma aminoacid level in the post-absorptive period in individuals receiving a series of controlled diets with different amounts of total nitrogen. With 7 g of nitrogen (i.e. 45 g of protein) in their diet, both age groups showed the same average plasma aminoacid level and also equal proportions of essential aminoacids. However, with 3.5 g of nitrogen in the diet, the amount of essential plasma aminoacids gradually fell during the 55 days of the test period. In this case, as the fraction of essential aminoacids (E) decreased, that of non-essential aminoacids (N) rose to such an extent that the total amount of aminoacids in blood plasma remained the same as before or slightly higher. The E/N ratio fell.

On the basis of these experiments, the author concludes that the decrease of the E/N ratio in plasma is associated with prolonged feeding on low-protein diets.

Other workers[55] also showed (on 6 women) that a decrease of the E/N ratio in the plasma to 0.3 and below is evidence of inadequate protein intake. In general, the E/N ratio can serve as an indicator of the protein nutritional status of man[57]. Czech biologists[56] proposed a simplified method for the determination of the E/N ratio in blood plasma (the so called Whitehead test) in healthy and sick people.

The experiments of Nakagawa and Masana[58] on healthy young people showed definite changes in the aminoacid composition of plasma due to an increase in the amount of free aminoacids associated with a deficiency of protein or free aminoacids in the diet. This phenomenon may serve as a test for a subclinical nitrogen deficiency, indicating an enhanced decomposition of tissue proteins.

On the other hand, a specific deficiency of a particular essential aminoacid was not determined. Swendseid investigated this problem too. Measurements were made of the amount of plasma aminoacids after the intake of a diet with a deficiency of any one aminoacid. It was found that, when the amount of lysine in the diet was reduced to about 50% of the requirement, the lysine level in the plasma remained unchanged. Even in its complete absence (less than 100 mg in the total diet), there was no change either in the amount of plasma lysine or in the E/N ratio.

Analogous results were obtained for phenylalanine and tyrosine[59]. Valine deficiency was investigated on two subjects. In one a decrease in plasma valine after the intake of 60% of the level of control valine was observed after 5 days, while in the other the same decrease was noted towards the end of the second day of the experiment. From this, one may conclude that the dietary deficiency of some aminoacids has a more rapid effect on their level in the plasma than for others, which is probably associated with the different metabolic pathways of these aminoacids.

When Rose tested on human beings various aminoacid mixtures, he noted that the deficiency of certain aminoacids did not have an appreciable effect, while the deficiency of others caused vomiting, loss of appetite, irritability, etc.

It is interesting to elucidate whether the deficiency of dietary aminoacids causing these symptoms in man is linked to a change in their plasma level. Then, by controlling the level of aminoacids in plasma, it might be possible to eliminate these undesirable phenomena. A considerable influence of the correct ratio of essential and non-essential aminoacids (E/N) in the diet on the aminoacid composition of the plasma and the growth of animals has been noted.

Young and Zamora[44] found that the optimum E/N ratio in the diet is in the range 1.0–2.66. Harper and Stucki[70] believe that a range between 1 and 4 is possible.

In their extensive review dealing with the role of essential aminoacids in nutrition, Swaminathan and Daniel[61] quote numerous data in favour of the ratio E/N = 1, i.e. the same as that found in chicken egg protein. This E/N ratio is preferable in the diet of children and growing animals, while in adults the nitrogen balance is maintained with E/N = 2:1.

It has been established[62] that, when the total nitrogen content in food is higher, maximum growth is attained with a smaller fraction of essential aminoacids. Thus by increasing the total nitrogen level with the aid of cheap non-specific nitrogen sources, it is possible to achieve the "preservation" of essential nitrogen, i.e. essential aminoacids.

V. THE ROLE OF NON-SPECIFIC NITROGEN AND ITS FORMS

The relatively low requirement by man for essential nitrogen permits the "dilution" of first-class protein by cheap forms of non-essential nitrogen. Kremer[63] emphasises the dual function of non-essential nitrogen in the organism: (1) the provision of material necessary for the synthesis of nitrogen compounds; (2) the prevention of the use of essential nitrogen for these purposes.

The question arises of the form in which non-essential nitrogen is most fully utilised by the organism. It has been found that it can be provided either as a mixture of all the non-essential aminoacids which enter into the composition of a particular natural protein, or as various ammonium and urea salts, or as a single aminoacid, etc.

Watts et al.[64] investigated the relation between the retention of nitrogen, the excretion of ammonia, and the source of non-essential nitrogen. The retention was best on feeding with a mixture of 8 non-essential aminoacids: alanine, arginine, glycine, histidine, proline, serine, and aspartic and glutamic acids, in proportions corresponding to those in beef. Large losses of nitrogen with urine were observed during the intake of proline, histidine, or arginine. The losses with urine were higher during feeding with arginine alone and lower during feeding with histidine, compared with the mixture of non-essential aminoacids. The level of blood ammonia was higher on feeding with glycine alone than on feeding with the aminoacid mixture.

These data are consistent with those presented in the report by Swendseid quoted above. The unsuitability of the replacement of an aminoacid mixture by glycine alone was clearly demonstrated on four adult subjects. However, a 1:1 mixture of glycine and diammonium citrate proved to be a complete replacement for a mixture of 7–8 non-essential aminoacids.

On the other hand, Snyderman et al.[65] demonstrated on unweaned infants that the replacement of 74% of the milk nitrogen by glycine alone does not have a negative effect on the rate of their growth.

Huang et al.[66] investigated on 9 male students the degree to which beef protein can be replaced by an equivalent amount of non-specific nitrogen. The latter (equal amounts of glycine and diammonium citrate) could constitute up to 20% of the basic diet in all 9 subjects without undesirable consequences.

A dependence of the effectiveness of the utilisation of non-specific nitrogen on the total nitrogen level has been noted[67]. This observation was confirmed also by Kies et al.[68]: each of 6 young men received 4 g, 6 g, and 8 g of total nitrogen per day during 3 experimental periods, each lasting 12 days, 1.12 g of nitrogen being in the form of all 8 essential aminoacids, the non-essential aminoacids cystine and glycine, and diammonium citrate. The nitrogen balance was negative with 4 and 6 g of total nitrogen. An increase of nitrogen intake from 4 to 6 g reduced the nitrogen deficiency in 4 out of 6 cases, while an increase of the intake from 6 to 8 g improved the balance in all cases. Kies et al.[69] investigated the optimum amounts of non-specific nitrogen for the retention of nitrogen by the organism of adult human beings under conditions where the essential aminoacids were provided by whole cereal protein. Best retention of nitrogen was achieved when the level of total nitrogen was 12.68 g per day, 6.0 g comprising non-essential nitrogen.

Many investigators have paid more attention to the qualitative composition of non-essential nitrogen than to

its quantitative amount in the diet. It has been shown that not all sources of non-essential nitrogen are equivalent[70]. The key position of glutamic acid in nitrogen metabolism has long been known, while the role of hydroxyproline is insignificant. In many cases the addition of serine and cystine actually has a toxic effect[71].

The inclusion of asparagine in aminoacid mixtures plays a favourable role in their effective application[72,73]. Urea as a possible source of food nitrogen is also of interest. There are data showing that, like animals, man has the enzyme urease, which cleaves urea to ammonia and carbon dioxide[74].

Snyderman et al.[65] investigated the nitrogen balance and the gain in body weight in children receiving 1.1 g of milk protein per kilogramme of body weight with the addition of urea as a source of non-essential nitrogen. The results showed that the urea additive favoured an increase in body weight and in the retention of nitrogen. At the same time urea has been found to have a toxic effect on the human organism[75]. Despite these findings, urea will probably not find wide application in synthetic diets for man.

One may assume that, although the role of non-essential aminoacids in protein nutrition has been investigated in fair detail on animals and man [65,68,76], the determination of a quantitative relation between essential and non-essential aminoacids in the diet requires further work.

VI. AMINOACID MIXTURES TESTED ON MAN

Harker et al[77] suggested that, in a study of the effect of the balance in mixtures, the latter must be constituted on the basis of the composition of the tissues and body plasma. The investigation of various combinations of aminoacid mixtures, made up in proportions according to the natural proteins in human nutrition selected as models, has been the subject of numerous publications. Thus, in experiments on 6 women, Kirk et al.[78] demonstrated a higher effectiveness of a mixture of aminoacids in the proportions in which they are contained in milk proteins and in peanut oil compared with the effectiveness of the set of aminoacids proposed by FAO. In analogous experiments on the same number of female patients, Leverton and Steel[26] did not find any difference in the retention of nitrogen for two aminoacid diets: one based on the FAO standard and the other based on the composition of oat protein with the addition of limiting aminoacids. A similar comparison was also made by Swendseid et al.[79] They investigated on 10 young women (18–25 years) the effect of diets made up of a mixture of pure aminoacids according to the FAO standard and on the basis of the composition of the chicken egg. The results are presented in Table 3.

Best retention of nitrogen was observed for the aminoacid mixture based on the egg composition but the differences in the balances are small for the two mixtures. A clear difference between men and women as regards the requirement for total essential nitrogen has been found. In addition, the authors confirmed in experiments on women their previous observations on men, namely that the requirement for essential nitrogen is in no way related to body weight. The limits of the requirement for essential aminoacids established are between 0.65 and 0.85 g per day for women and between 1.0 and 1.3 g per day for men. However, it is so far unknown whether these differences are associated with different requirements for all these aminoacids or only with any one of them.

Clark et al.[81] showed that the requirement for lysine is the same for both sexes. Thus it is possible that the requirement for essential aminoacids in man is greater than in women owing to certain specific aminoacids.

Other investigators[80] showed that an increase in the content of essential aminoacids in the diet of 6 healthy males from 1.1 to 5.5 g per day (for an overall daily dose of 6 g of nitrogen) was accompanied by a progressive increase in the retention of nitrogen in the organism (on average by 1.9 g of nitrogen per day).

Table 3. The proportions of aminoacids and the daily intake of essential aminoacids based on the FAO composition and the set of aminoacids in egg protein.

L-Aminoacids	Aminoacid : L-tryptophan ratio		Tryptophan intake = 240 mg	
	FAO	egg	FAO, g/day	egg, g/day
Tryptophan	1.0	1.0	0.24	0.24
Isoleucine	3.0	3.7	0.72	0.89
Leucine	3.4	5.4	0.81	1.30
Lysine	3.0	5.4	0.72	1.09
Methionine and cystine	3.0	3.7	0.81	0.99
Phenylalanine and tyrosine	4.0	4.7	0.96	1.13
Threonine	2.0	3.1	0.48	0.74
Valine	3.0	3.9	0.72	0.93
Total essential nitrogen	—	—	0.63	0.86

In experiments on young men, Watts et al.[82] compared the effectiveness of three sets of aminoacid diets: (1) a diet based on the FAO standard: (2) a modified FAO diet; (3) a diet based on the wheat flour protein. The total nitrogen intake was 10 g in all cases. It was shown that the first two diets have the same biological value. When comparable amounts of lysine, a limiting aminoacid in wheat flour, were ensured in the FAO diet and in the diet based on the wheat flour model, the retention of nitrogen in both groups of men was the same. The limiting requirement for total essential nitrogen ensuring a slight positive nitrogen balance in men was established in this series of experiments as between 0.63 and 0.84 g per day, i.e. less than shown by Swendseid but higher than the minimum requirement according to FAO, which is suggested as 0.48 g per day.

According to the data of Swendseid et al.[83], the nitrogen balance in people receiving essential aminoacids in the same proportions as in plasma proved to be negative. It was established that in plasma the concentrations of valine and lysine are relatively higher than in food proteins and the contents of isoleucine and leucine are lower, and that this probably does not constitute optimum conditions for the anabolic processes in the organism.

As an example of an aminoacid diet successfully employed, we may quote that tested by Clark et al.[84] Apart from the essential aminoacids (taken in the proportions specified by Rose), the diet contained 130–140 g of white flour (in the form of biscuits and cake) and also dehydrated milk, cornstarch, sugar, and preserved fruit. The overall calorie content was 2100–3250 kcal.

Non-essential nitrogen (mg per day):

arginine	-620	aspartic acid	-850
histidine	-330	glycine	-580
alanine	-490	serine	-800
proline	-1820	glutamic acid	-5810

The amount of total nitrogen in different series of experiments was 4.5, 6, and 9 g. The amount of the basic mixture of essential aminoacids was increased by factors of 1.0, 1.5, 2.0, and 2.5 and the corresponding mean nitrogen balance was +0.07, +0.22, +0.56, and +0.72. It was found that a daily dose of total nitrogen of both 6 and 9 g is quite sufficient to maintain a positive nitrogen balance, while 4.5 g is clearly inadequate.

Table 4. An aminoacid diet for children (12 year old boys).

Aminoacid	Daily intake, g	N content, g	Aminoacid	Daily intake, g	N content, g
Essential L-aminoacids			Non-essential aminoacids		
Isoleucine	1.00	0.107	Alanine	9.22	1.449
Leucine	1.50	0.160	Arginine	10.81	3.476
Lysine	1.60	0.307	Aspartic acid	10.76	1.132
Methionine	0.80	0.075	Glutamic acid	10.76	1.024
Phenylalanine	0.80	0.068	Na glutamate	12.50	1.035
Threonine	1.00	0.118	Glycine	7.65	1.420
Tryptophan	0.12	0.017	Histidine	1.00	0.271
Valine	0.90	0.108	Proline	4.61	0.561
			Serine	6.92	0.922
			Total nitrogen		12.250 g

In their subsequent investigation Clark et al.[85] studied the effect of an increase of the amount of lysine in the mixture on the retention of nitrogen. The following amounts of lysine were added to the mixture (in place of the previous 1780 mg of lysine per day): 2900, 1800, 2700, and 3600 mg per day. The best retention of nitrogen was noted when the level of lysine was 3600 mg per day. Very valuable data have been presented by Nagakawa et al.[86], who investigated synthetic aminoacid diets on children. In earlier studies by these workers the minimum requirement by school age children for each essential aminoacid, determined separately, was established[87]. Then mixtures of the same aminoacids were made up. Tests were made on 5 boys, 10–12 years old, and were continued for 24 days. The basic diet contained a mixture of aminoacids, corn starch, corn and olive oil, mineral salts, and vitamins. The entire experiment was carried out in two periods: during the first period the total nitrogen intake was 12.25 g and during the second 10.23 g. The energy intake was between 53 and 75 kcal per kilogramme of body weight. The data are presented in Table 4. All the children remained healthy, retaining a constant weight and a good appetite. The average nitrogen retention varied from +0.68 to +1.36 per day. But, as stressed by the authors, a simple positive nitrogen balance is not sufficient for children, who require additional nitrogen for growth and development.

If one bears in mind that the body of 10–12 year old boys contains 3% of nitrogen and that they gain 3 kg in weight per year, the retention of nitrogen should increase by 90 g annually, i.e. by +0.25 g per day. However, an additional 50%, i.e. a total of +0.38 g per day, must be added as a reserve.

Comparison of the data obtained by these workers with the value +0.38 g per day shows that the aminoacid mixtures tested are quite suitable to support the life of children at the normal level.

The necessity for the presence of arginine in the diet is still questionable. The removal of arginine from the diet did not affect the nitrogen balance and also did not give rise to any clinical disturbances. As regards histidine, the authors do not share the view of Albanese, who believes that this is an essential aminoacid for children. The absence of histidine from the diet for 15 days of the experiment did not affect the nitrogen balance.

Cabalska[88] also demonstrated the successful application of aminoacid diets in the feeding of children. Mixtures of aminoacids in the feeding of unweaned infants proved to be particularly effective[89].

Abernathy et al.[90] investigated the nitrogen balance in 58 girls aged 7–9, whose daily doses of total nitrogen amounted to 86–460 mg per kilogramme of body weight. The authors present data concerning the minimum level of essential aminoacids which must be provided with the diet to maintain the nitrogen balance at the normal level (in milligramme per kilogramme of body weight per day):

isoleucine	-24	phenylalanine	-28
leucine	-45	threonine	-20
lysine	-29	tryptophan	-4.9
methionine + cystine	-21	valine	-31

These data were obtained on at least 6 subjects whose daily nitrogen intake was 104–135 mg per kilogramme of body weight.

The American Company Schwarz Bioresearch Inc. is marketing synthetic diets, which consist of aqueous solutions of chemically pure ingredients with a 50% content of dry substances. They are designed for the experimental feeding of both laboratory animals and human beings. The diets are sold in bottles or sealed tubes and if desired may be flavoured. Table 1 gives the composition of one of the diets used for human nutrition. Its calorie content is 1.9 cal ml^{-1}. The specific gravity of the solution is 1.18–1.20 and its pH is 4.85. In the preparation of diets of this kind, the order in which the components are dissolved is very important.

VII. AMINOACID IMBALANCE, ANTAGONISM, AND TOXICITY

When artificial aminoacid diets are made up, particular attention must be paid to the study of the phenomenon of the so called imbalance—the breakdown of the optimum proportions of the aminoacids in the diet, which may arise both in the presence of an excess and a deficiency of a particular aminoacid. The problem of imbalance was investigated in very great detail by Harper and Rogers[91-94]. The imbalance is expressed in a series of symptoms characteristic of a disturbance in nutrition, namely in the arrest of the growth of young organisms and a disturbance of the nitrogen equilibrium in adult organisms, in the fatty degeneration of the liver, in an increase of the number of leucocytes in the blood, in albuminuria, and frequently in convulsions, vomiting, nausea, and other undesirable symptoms.

Some workers believe that an imbalance occurs also when even a slight excess of one or several aminoacids is added to the diet. Such an imbalance is usually less dangerous than in the absence of a particular aminoacid. Harper does not regard such a state as imbalance at all but attributes it to the antagonism and toxicity of aminoacids.

Sauberlich[95] made a comparative study of the toxicity and antagonism of 19 aminoacids fed under different conditions to young weanling rats. All 19 aminoacids were added in an amount of 5% of the weight of the diet, at a low overall nitrogen level. With the exception of alanine, all the aminoacids caused an arrest of growth to different extents.

An excess of methionine caused the most acute toxic effect. It is followed in decreasing sequence by tryptophan, aspartic acid, histidine, tyrosine, phenylalanine, cystine, leucine, valine, isoleucine, glycine, asparagine, arginine, lysine, and threonine. Glutamic acid, proline, and serine caused only a slight arrest of growth.

Antagonism can also occur in the interaction of the following pairs of aminoacids: leucine–isoleucine, isoleucine–valine, isoleucine–phenylalanine, phenylalanine–valine, phenylalanine–threonine, arginine–lysine.

The inclusion of an excess of leucine in a casein diet[94] arrests growth. The addition of isoleucine and valine, neither of which is limiting in this diet, prevents or decreases the arrest of growth, while the addition of threonine, a limiting aminoacid, does not have an effect. The absence of a response to the addition of the limiting aminoacid makes it possible to distinguish antagonism from imbalance. Thus antagonism constitutes the elimination of a harmful effect of an excess of one aminoacid by another with a similar structure, which, however, is not limiting in the given diet.

By virtue of the similarity of their structures, the antagonistic aminoacids probably interfere with one another during transport into the cells and disturb the enzyme equilibrium necessary for protein synthesis.

The toxic responses of the organisms are variable, including the cessation of growth and also irreversible functional and organic disturbances in many organs. Thus a dietary excess of tyrosine (more than 3%) causes an acute affection of the eyes and paws of young growing rats[94]. An excess of methionine completely suppresses growth and causes the atrophy of the cells in certain organs. An excess of phenylalanine interferes with the function of the brain[95].

Doolan et al.[96] observed a severe toxic response in man, expressed in ammonia intoxication following the intravenous injection of a 5% solution of glycine.

There are data[97] showing that sodium monoglutamate, widely used in the Chinese and Japanese cuisine as a taste improving additive to various dishes, causes an illness called the "Chinese restaurant syndrome" expressed in headache, a burning sensation in the stomach, and an increased [blood] pressure. This effect of sodium glutamate is associated with a specific dose. There exist appreciable deviations in the oral threshold doses for different individuals. The syndrome is caused by the following substances: sodium monoglutamate (3 g), potassium mono-L-glutamate (4 g), DL-glutamic acid (5 g), and L-glutamic acid (5 g). The syndrome is not caused by sodium mono-D-glutamate (7 g), sodium mono-L-aspartate (5 g), sodium chloride (10 g), and glycine (5 g). After the intravenous administration of sodium monoglutamate the symptoms occur even with a dose of 50 mg. However, there are doubts whether these may not be the effects of the enhanced sensitivity of the test subjects.

Bearing in mind that L-glutamic acid is a normal metabolic product, the official international medical organisations object to any limitations to the use of sodium glutamate as a taste additive[98].

The above examples of the effect of the toxicity of aminoacids on animal and human organisms make it necessary to refine the dosage in such a way that acute toxicity does not occur. Acute toxicity is understood as entailing the death of all the animals receiving the lethal dose (LD) of aminoacids. The dose which leads to the death of 50% of the animals receiving the test diets is also regarded as lethal, is denoted by LD_{50}, and is defined as follows:

$$LD_{50}=x_s-d\,(\Sigma p-{}^1/_2)^{99},$$

where x_S is the dose for which all the animals die, d the interval between the specified doses, p the ratio of the number of dead animals to the particular dose, and Σp the sum of all the ratios of the numbers of dead animals to all the doses administered to them[99].

As long ago as 1955, Greenstein and coworkers[100] put forward the problem of acute toxicity in the comparison of L- and D-forms of aminoacids. Examples of the comparative toxicities of the DL-, D-, and L-forms of certain aminoacids are presented below:

Aminoacid	LD_{50}, g kg^{-1} for		
	DL-	L-	D-
Methionine	5.95 ± 0.04	4.3	5.2
Threonine	5.85 ± 0.04	3.1	5.3
Valine	6.25 ± 0.05	5.4	6.1

Molle[99] noted that, in respect of acute toxicity, racemic forms are less toxic than the L-forms. On the basis of numerous experiments on laboratory animals, the author concludes that even high doses of the D-isomers have a less toxic effect than the corresponding L-forms. These conclusions are in conflict with the views of Elvehjem[101], who attributes especially high toxicity to racemic aminoacids[101].

Probably D-isomers do not have any unfavourable effects and are simply unused by the organism. Sauberlich also showed that the D-isomers are less toxic than the L-forms. However, DL-aspartic acid has a more harmful effect than the L-isomer. The L- and D-forms of tryptophan have the same toxic effects[95].

Studies on these lines should be continued in the first place, since large-scale application of aminoacids in the food industry will become possible only after an accurate determination of the aminoacid norms in the diet which do not give rise to any acute or toxic effects.

Shtenberg and Ignat'ev[102], who examined the principles of the study of toxicity, recommend that for greater reliability the experiments be performed on three animal species, one of which must be a rodent. It is necessary to test a large number of animals in each group: not less than 100 mice, 50 rats, 100 chickens, 25 guinea-pigs, 3 dogs, and 15 rabbits. The concluding stage of the investigations should involve experiments on volunteers (10–20 people), who should receive the test diet over a period of 10–30 days.

The observation of the initial stage of the changes occurring in the organism under the influence of the experimental diet is of great interest. In a short experiment on rats, Sanahuja and Rio[103] carried out biochemical studies in order to distinguish the initial stage of the changes due to the intake of a non-balanced aminoacid mixture. An increase in the amount of protein, amino-nitrogen, and the content of threonine in the liver was

noted. Probably the initial imbalance is associated with a more rapid protein synthesis in the liver and also with an increase of the glycogen content in the latter. The same phenomenon was also observed by other workers[104,105].

L-Tryptophan causes the accumulation of neutral fat in the liver in the course of 2.5 h after its introduction into the rat organism. The introduction of other aminoacids such as L-methionine, L-lysine, L-tyrosine, and L-threonine did not increase the amount of fat in the liver. The introduction into the organism of ATP, ADP, AMP, adenosine, or folic acid together with L-tryptophan prevents the generation of fat in the liver. Probably the generation of fat caused by L-tryptophan is associated with a decrease of the amount of ATP, whose effect is suppressed when L-tryptophan is administered.

Hunter et al.[105] observed an increase in the amount of liver glycogen after feeding with added glycine and L-tyrosine. This was eliminated by including D-tyrosine in the diet.

Murata et al.[106] noted a favourable effect of L-threonine (but not D-threonine), introduced in an amount of 0.2% of the weight of the diet, in preventing the accumulation of fat in the liver caused by the dietary imbalance.

The metabolic rearrangement shown as a response to the consumption of a non-balanced aminoacid mixture by man was investigated by Soliman[107]. All the investigators studying the aminoacid imbalance note a favourable effect of protein added to the diet.

In experiments on weaned rats with three protein levels in the diet (6, 9, and 12%), Harper et al.[108] showed that 12% of protein prevents the harmful effect of the excess histidine and tyrosine in the diet. Added protein has a similar effect also in the presence of an excess of methionine and threonine.

A high aminoacid content in the diet does not by itself have a toxic effect[109]. In fact rats can digest large amounts of aminoacids in the presence of 80–90% of protein in the diet without an appreciable arrest in growth. This observation is confirmed by the diet of specific groups of men containing up to 200 g of protein per day. Certain Australians, the Gaucho in the South American prairie, and the Masai tribe in Central Africa retain satisfactory wellbeing on a diet of 250–300 g of protein per day.

A characteristic sign of imbalance is a reduced requirement for food. Sometimes it is difficult to conclude whether the decrease of the effectiveness of the nitrogen intake is linked directly to a toxic effect or whether this is a secondary factor, while the primary factor is the reduced requirement for food.

A stimulation of food intake and growth can be achieved by the introduction of insulin[110] and cortisol[111] and also by maintaining the animal at a reduced temperature[112]. One may conclude from this that a principal cause of the arrest of growth in animals receiving non-balanced diets is a decrease of the requirement for food.

The reduction of the requirement for food can reach up to 50%.[113] Leung and Rogers conclude that the central nervous system probably contains receptors sensitive to the concentration of the essential aminoacids in blood plasma.

Arginine plays a positive role in the utilisation of non-balanced diets[114,115]. It reduces the imbalance caused by an excess of the following aminoacids: lysine, tyrosine, histidine, glycine, methionine, cystine, valine, threonine, isoleucine, and phenylalanine. The addition of arginine in an amount of 0.3–2.0% of the weight of the diet eases the imbalance due to the aminoacids enumerated above but does not eliminate the imbalance caused by tryptophan, leucine, and glutamic acid.

Hepburn and Bradley[31] also confirm the idea that the function of arginine and glutamic acid consists in a weakening of the potential toxicity of ammonia arising on feeding large amounts of aminoacids. In this respect glutamine is more effective than glutamic acid. The attempts to determine the role of arginine in the detoxication of an excess of aminoacids have so far been unsuccessful. After a time the imbalance phenomena decrease, which is evidence of a gradual adaptation of the organism.

VIII. ENRICHMENT OF SECOND-CLASS PROTEINS BY THE ADDITION OF AMINOACIDS

It is also necessary to take into account the aminoacid balance in the addition of synthetic aminoacids to second-class plant proteins, such as those derived from wheat, corn, rice, millet, etc. with the aim of increasing their biological value. Similar additives constitute a valuable contribution by aminoacids to human nutrition.

McPherson has noted[116] that, in order to cover the deficit in food products by 1980, it will be necessary to produce an additional 18 million tons of fat, 9.9 million tons of animal protein, and 11.4 million tons of aminoacids. The total amount of aminoacids necessary for addition to human food in underdeveloped countries is 0.5–1.0 million tons per year. The total consumption of protein in Asia, Africa, and Central America reaches only 48–54 g daily per man, while the minimum requirement is 60 g. The greatest world deficiency is experienced in respect of three essential aminoacids—methionine, lysine, and tryptophan.

In 1966 the American Chemical Society[117] examined widely the problem of the sources of additional protein. The following sources of this kind have been suggested: various oil bearing plants (cotton seeds, peanuts, coconuts, sesame, sunflower, etc.), threshed wheat fractions previously employed as cattle-feed, defatted dry milk, various protein concentrates, such as, for example, fish protein or soya protein concentrate.

The problem of the aminoacid additives was specially examined and their advantages compared with the use of protein concentrates for the enrichment of second-class proteins was noted. Chemically pure aminoacids are added in small amounts and therefore cannot affect the organoleptic properties of cereal proteins. The quality of cereal proteins is then enhanced and they are more easily assimilated owing to the improved aminoacid balance. On the other hand, the amount of additive is smaller than in the case where protein concentrates are added.

The amounts of each aminoacid to be added to human food in practice still requires a more accurate determination.

Prolonged experiments on man can help discover the necessary amounts for such enrichment. Howe and coworkers[118,119] showed that aminoacid additives, including lysine, tryptophan, and threonine, improve the quality of proteins, for example those in cereals, making them equivalent to casein.

The amounts of aminoacids employed vary in the range 0.1–0.4% of the total weight of the diet. Tryptophan is an exception—not more than 0.07% should be taken.

In order to evaluate a particular protein and to establish the aminoacid in which it is deficient, Block and

Mitchell introduced the concept of the "chemical score" of the protein. With the aid of this concept, it is possible to compare the aminoacid composition of any protein with that of a protein adopted as a standard. The whole chicken egg is regarded as an ideal protein both as regards composition and its aminoacid balance. Therefore the percentage content of each aminoacid in the test protein is compared with that in the chicken egg. Then the aminoacid which, in relation to its amount in the egg protein, is present in the smallest quantity is regarded as the first limiting aminoacid of the test protein. Its ratio in the two proteins is in fact the "chemical score" of the given protein.

For example, lysine is present to the extent of 2.7% in wheat protein and 7.2% in egg protein. The ratio $\frac{\text{wheat lysine}}{\text{egg lysine}} \times 100 = 37$. Thus the deficiency of wheat lysine is $100-37 = 63\%$ relative to egg protein.

Yuyst, Arnould, and coworkers[120,121], who for many years have been concerned with the problem of the improvement of the biological value of proteins by the addition of synthetic aminoacids, suggest that, before introducing each additive into the cereal protein diet, one should establish accurately the first limiting factor of the given protein, and this should in fact be the first additive. The same authors showed the effectiveness of the addition of lysine to white flour. If the "white flour–lysine" mixture is treated further with threonine and isoleucine together, the latter have an additional improving effect, but this does not occur if the aminoacids are added separately. The addition of valine, methionine, and cystine together or without lysine did not produce any results. Consequently here a clear non-equivalence of particular aminoacids is shown, which gives rise to the problem of further improvement of the necessary norms in the addition of aminoacids to protein.

Lysine and methionine are now manufactured on an industrial scale and their addition to food does not present difficulties; on the other hand, threonine and tryptophan are obtained only in small amounts.

Nevertheless the advances in the chemical synthesis of all the essential aminoacids give rise to hope that the problem of obtaining cheap aminoacids will be solved in the near future[122]. The techniques used to enrich cereal protein by synthetic aminoacids are various[123].

When cereals are employed in the form of ground flour or granules, the enrichment is carried out directly by mixing in the aminoacids. The added aminoacids should be ground to the same particle size as the bulk of the flour. The technique becomes more complicated when the cereals are employed in the form of whole grains. Crystalline pure aminoacids can then be introduced as granules resembling particular grains. When protein concentrates are introduced, the ratio of the true and artificial grains is 20:1 or 30:1 and when aminoacids are added the ratio is 200:1.

Graham[124] investigated the enrichment of wheat used in the form of grains. He suggests various envelopes and also grain imitation. Lysine is added by spray drying and also by a "steeping" technique. Additional work is required to determine whether this lysine can withstand treatment of any kind (mechanical or thermal) during the preparation of fortified flour.

Pokrovskii et al.[125] investigated the effectiveness of the addition of L-lysine hydrochloride to improve the nutrient value of wheat bread. The optimum dose of the preparation (0.25–0.5%) relative to the total weight of the flour used to make the bread was established. The bread should be baked at a temperature reduced by 20–25°C.

Koz'mina's review[126] deals with the improvement of the nutrient value of the grains and the development of "synthetic" grains. Gololobov[127] deals with the problem of the enhancement of the nutrient value of protein by synthetic aminoacids with the aim of increasing the protein resources not only of backward but also of advanced countries. A successful use of aminoacid additives to cereal proteins in children's diet has been reported by Bressani et al.[128]

Parthasarathy et al.[129] added DL-methionine to the diet of children 8–9 years of age, which led to an appreciable improvement of the biological value of the proteins. In this respect, the hydroxy-analogue of DL-methionine is less effective[130].

Other Indian workers[131] suggest that methionine and lysine be added to children's food comprising a soya bean–sesame mixture.

Cantor and Roberts[132] reported an improvement of the quality of the protein in corn food products. They discussed mixtures of corn with various proteins and aminoacids, particularly lysine and tryptophan. Kies et al.[133] established that lysine is the limiting aminoacid in corn.

In a study of a plant mixture containing 47% of autho-clave-treated chick peas, 35% of defatted sesame flour, and 18% of soya bean flour, Guggenheim and Szmelcman[134] showed that it is less effective than casein. The addition of lysine improves its value. However, its value does not alter on addition of either methionine or tryptophan. The addition of threonine together with lysine did not affect the effect of the latter, while methionine reduced it.

Despite the abundance of studies demonstrating the value of aminoacid additives to second-class proteins, there are also others—for example, Hegsted[135] believes that the use of products of this kind is still untimely and uneconomical. The author voices the fear that there are still no quantitative data concerning the optimum content of aminoacids in a particular diet and that they should not be used, particularly in the food of children.

Apart from being used in the food industry to improve the biological value of cereals, mixtures of aminoacids can also be used to enhance and improve the taste of many food products. The literature quotes aminoacids which, when mixed in appropriate proportions, can produce the taste of the following products: onions[136], crab[137], fish[138], soya sauce[139], and chicken and meat broth[140]. Chemically pure aminoacids have the following intrinsic flavours: none (tasteless) (D- and L-alanine, D- and L-arginine, D- and L-aspartic acid, D-glutamic acid, L-histidine, D- and L-isoleucine, D- and L-lysine, D- and L-proline, D- and L-serine, D- and L-threonine, and D- and L-valine), sweet (D-tryptophan, D-histidine, D-phenylalanine, D-tyrosine, D-leucine, L-alanine, and glycine), bitter (L-tryptophan, L-phenylalanine, L-tyrosine, L-leucine), and with a slight sulphurous flavour (D- and L-cysteine and D- and L-methionine).[141]

IX. AMINOACIDS IN MEDICINE—WITH PARTICULAR REFERENCE TO PARENTERAL FEEDING

The use of aminoacids in medicine must be regarded as a special case of their employment in human food. Pokrovskii notes several applications of aminoacids in medicine[142]. Various aminoacids are used in the therapy of many diseases. L-Lysine is very effective in the feeding of premature babies. L-Methionine, which

exhibits lipotropic activity, is indicated in the treatment of the cirrhosis of the liver.

In addition methionine is used in the surgical traumas of the heart, in the myocardial infarct, and also in thyrotoxicosis. There has been a general accumulation of definite data concerning the effect of aminoacids on cardiac function. Thus DL- and L-methionine and L-leucine intensify cardiac contractions, while aspartic and glutamic acids and arginine have an inhibiting effect[143].

The cause of a number of psychoneurotic disorders is an innate disturbance of the aminoacid metabolism (phenylpyruvic oligophrenia, the glycine disease, argininosuccinicaciduria, and Hartnup disease). L-Glutamic acid is used in the treatment of many psychological illnesses, for example, in epilepsy. Efron[144] quotes a list of 14 diseases caused by a disturbance of the aminoacid metabolism; 12 of these are expressed in psychological disorders. Many of these diseases are susceptible to treatment with the aid of aminoacid diets and by vitamin therapy.

A classical example of the successful application of an appropriate aminoacid diet is the treatment of phenylketonuria[145]. The exclusion of phenylalanine from the diet of patients maintains a normal state.

Artificial aminoacid mixtures are also used to feed patients by the intravenous injection of a solution of these aminoacids, i.e. parenterally. Parenteral feeding is indicated in most cases where feeding *per os* is impossible or endangers life. Experimental clinical studies showed that total parenteral feeding using a mixture of aminoacids, glucose, and lipid emulsions can maintain a satisfactory nutritional state in the majority of patients.

In parenteral feeding one usually employs (1) enzymatic hydrolyzates of various proteins, primarily casein, and (2) mixtures of synthetic crystalline aminoacids in the L- and DL-forms containing all the essential aminoacids and some source of non-essential nitrogen (mainly glycine). The D-forms are usually not utilised by the organism and their inclusion in such mixtures is undesirable.

Aminoacid mixtures have the advantage of purity over hydrolysates (inadequately dialysed enzymatic hydrolysates can contain peptides capable of inducing an allergic response) and also there is a possibility of varying their composition depending on the physiological state of the patient.

As early as 1940, Shohl and Blackfan[146] were the first to use an aminoacid mixture for complete parenteral feeding. Since then, this field of medicine has been successfully developing in a number of countries: Sweden, Denmark, Germany, France, Italy, and Poland[147-155]. In the USSR Latvian scientists have been successfully working in this field under the supervision of A. A. Shmidt[156,157].

In 1960 Geyer[158] published an extensive review on the application of parenteral feeding. Trémolières[159] quotes examples of the most thoroughly investigated aminoacid mixtures for parenteral feeding (Table 5).

The limiting aminoacid in the majority of preparations is isoleucine[160]. The problem of the addition of non-essential aminoacids in parenteral feeding has so far been inadequately investigated.

Satisfactory proportions of the aminoacids, similar to those in first-class proteins such as those of milk, eggs, and meat, have been found in the enzymatic hydrolysate of the yeast *Candida tropicalis* and in the product obtained from it after purification and consisting of a mixture of aminoacids and lower peptides[161].

A synthetic aminoacid mixture marketed by the Japanese firm Ajinimoto Co. under the conventional name "aminoacid substances" is used as a highly nutritive food product (in the form of tablets) or as a substitute for blood plasma (in the form of a sterile solution). The mixture contains 16 aminoacids and its composition is as follows (%):

alanine	6.0-7.4	lysine	11.5-14.5
arginine	4.6-6.0	methionine	1.0-1.2
aspartic acid	5.8-7.4	phenylalanine	4.3-5.3
glutamic acid	9.0-11.8	proline	4.2-5.2
glycine	4.0-4.8	serine	3.5-4.5
histidine	3.2-4.0	threonine	3.0-3.6
isoleucine	4.4-5.4	tyrosine	1.0-1.2
leucine	8.4-10.4	valine	4.1-5.1

Table 5. The most thoroughly investigated aminoacid mixtures for parenteral feeding (aminoacids contents expressed as percentages of the dry substance).

Name	Amigène	Merck soln.	Parenamine	Aminosol	Travamine	Trophysan
Total nitrogen	12.9	13.3	13.7	13.4	12.0	15.2
Amino-nitrogen (% of total nitrogen)	75	100	93	69	65	100
Ash	5.5	1.0	—	—	—	1.2
Arginine	3.2	2.5	3.2	4.8	3.8	—
Isoleucine	4.9	8.0	4.5	3.8	3.0	3.2
Histidine	1.0	4.2	2.0	2.0	2.1	—
Leucine	9.1	16.5	6.0	5.6	7.5	5.1
Lysine	5.1	9.4	5.8	7.0	6.8	7.9
Methionine	2.6	4.0	3.7	2.8	1.1	5.2
Phenylalanine	3.9	4.3	2.8	3.0	3.2	4.4
Threonine	2.9	1.9	2.3	5.2	5.3	3.2
DL-Tryptophan	1.3	0.9	1.3	0.9	1.0	1.9
Valine	5.3	7.0	4.7	4.0	5.8	4.4
Glutamic acid	17.1	1.5	—	10.6	10.9	—
Tyrosine	4.6	0.3	1.4	2.6	0.9	—
Glycine	0.4	23.0	—	5.6	—	59.5
Aspartic acid	4.7	0.2	—	5.2	8.1	—
Proline	6.2	—	—	5.8	—	—
Serine	4.9	—	—	5.8	—	—
Alanine	4.2	—	—	3.8	—	—
Hydroxyproline	1.5	—	—	—	—	—
Cystine	0.3	—	—	2.4	2.1	—

Among non-essential aminoacids, best results are given by glycine and glutamic acid. Furst et al.[147] showed that glycine is a necessary source of non-essential nitrogen when essential aminoacids and arginine are administered. This investigator demonstrated the higher effectiveness of a mixture of crystalline aminoacids compared with hydrolysates in the parenteral feeding of surgical patients, while in healthy people a positive nitrogen balance is most pronounced when casein hydrolysates are administered. He also established that the nitrogen balance increases when a mixture of glycine, L-alanine, and L-proline serves as a source of non-essential nitrogen and therefore he believes that alanine and proline are semi-essential aminoacids, the introduction of which into the mixture for parenteral feeding is necessary.

Table 6 gives the compositions of the USSR preparations for parenteral feeding. The data show that in all the preparations an approximately 50:50 ratio of essential and non-essential aminoacids is maintained[162].

Deligné and Wretlind[163] believe it useful to employ a mixture of these non-essential aminoacids rather than other sources of non-essential nitrogen. Breinlich[164] also thinks it necessary to include in the mixture L-histidine,

L-arginine, and vitamin B, sorbitol, and mineral salts in addition to the eight essential aminoacids.

Heller et al.[150] demonstrated that the aminoacids in solutions prepared from casein hydrolysate are better assimilated than the aminoacid mixtures made up in accordance with the composition of plasma. These data are consistent with the ineffectiveness, mentioned above, of the aminoacid mixture based on the plasma model and designed for peroral feeding.

Table 6. Aminoacid composition of protein hydrolysates produced in the USSR for parenteral feeding.

Aminoacid	Aminoacid composition, g per 100 g of conventional protein				
	Aminopeptide	L-103	TSOLIPK hydrolysate	Aminokrovin	Fibrinosol
Phenylalanine	5.8	6.5	4.6	6.8	4.6
Tyrosine	1.2	2.3	3 9	2.2	3.2
Total aromatics	7.0	8.8	8.5	9.0	7.8
Methionine	1.02	1.1	2.1	1.1	2.1
Cystine	1.83	1.3	1.1	1.1	2.1
Total sulphur-containing acids	2.85	2.4	3.2	2.2	4.2
Threonine	4.6	4.9	3.9	4.7	6.8
Tryptophan	2.1	0.5	0.5	0.4	1.2
Valine	9.3	9.1	7.7	10.8	4.8
Lysine	10.1	13.1	9.3	11.3	12.8
Leucine	11.8	12.7	9.1	13.8	8.2
Isoleucine	1.80	1.4	5.9	1.10	4.0
Total essential aminoacids	49.55	52.9	48.1	53.3	49.8
Arginine	4.9	4.8	3.7	3.4	7.0
Histidine	4.7	6.4	4.1	8.3	5.9
Alanine	8.2	9.4	3.1	10.2	4.4
Glycine	4.5	4.7	2.2	4.8	7.5
Serine	4.8	5.6	3.8	3.9	6.7
Proline	3.6	3.0	11.0	4.7	7.4
Glutamic acid	8.4	6.3	15.0	3.7	5.5
Aspartic acid	9.8	6.3	4.3	4.4	1.7
Total non-essential aminoacids	48.9	46.5	47.2	43.4	46.1
Total	98.45	99.4	95.3	96.7	95.9

As in peroral feeding, when an aminoacid solution is introduced intravenously, the correct ratio of total nitrogen to carbohydrates and fats must be rigorously observed and the amounts must be sufficient for the energy needs of the organism.

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Summarising the literature data discussed above, certain fundamental conclusions may be made.

1. Aminoacid mixtures based on the composition of first-class food proteins probably constitute an adequate substitute for meat, milk, fish, etc. proteins. Man can subsist for a long time on a diet containing aminoacids with the addition of fats, vitamins, carbohydrates, and mineral salts. The physiological and biochemical parameters are then maintained at the normal level.
2. It is useful to improve the biological value of plant proteins to the level of highly effective animal proteins by the addition of chemically pure aminoacids. It is then necessary to observe the correct aminoacid balance in the overall fortified protein because the breakdown of such balance is in fact primarily responsible for the inadequacy of a particular diet.
3. The aminoacid mixtures introduced into the organism parenterally in the form of solutions constitute an excellent means for the maintenance of a sick organism incapable of food intake in the usual manner for one reason or another. This does not exhaust the applications of aminoacids in medical practice. There are many diseases which are susceptible to treatment by specially compounded aminoacid diets and by vitamin therapy.

In all cases, before the direct application of aminoacid mixtures in human nutrition, it is necessary to test them carefully on experimental animals and volunteers to avoid toxic or allergic effects of the artificial diet. However, science has now at its disposal data showing that there is no reason to over estimate the toxicity, since it can be avoided by the simultaneous introduction into the artificial mixture of appropriate amounts of arginine and glutamate and also by observing the appropriate balance of all the mixture components. When protein hydrolysates are used as food products, particular attention must be paid to the removal of impurities.

It follows from all the foregoing data that individual aminoacids can be used in human nutrition. They will probably play a significant role in increasing the food resources.

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Surface Layer Sorbents in Gas Chromatography

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The methods of preparation, chromatographic properties, and applications of surface layer sorbents have been examined. Chromatographic columns with surface layer sorbents are characterised by a low value of HEPT (0.4-0.5 mm) and a weak dependence of HETP on the flow rate of the carrier gas and the grain diameter of the solid carrier. Compared with the usual (bulk phase) sorbents, the use of sorbents of this new type makes it possible to shorten the duration of analysis by a factor of 3-15, to decrease the experimental temperature by 30-100 deg, and to extend the range of compounds susceptible to analysis.
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I. INTRODUCTION

The improvement of the separation of compounds with similar properties depends in many ways on the efficiency of the columns employed and therefore an increase in column efficiency is one of the important tasks of modern gas chromatography. One of the principal causes of the spreading of chromatographic zones, particularly at high carrier gas flow rates, is the resistance to mass transfer, the magnitude of which is known to depend on the grain diameter of the sorbent employed.

The sorbents used in gas chromatography usually consist either of a solid carrier covered more or less uniformly throughout the entire bulk by a liquid phase (the absorbent) or a porous adsorbent, the adsorption properties of which are also approximately the same throughout the bulk of the grain. During recent years sorbents in which the active substance (the sorbent) are not uniformly distributed throughout the bulk of the grain but only on its "outer" surface have come to be used in gas chromatography; the active substance is not present in the bulk of the grain and consequently the compounds chromatographed are not sorbed there. The sorption processes in such sorbents occur only in a surface layer of small depth equal to the depth of the layer of the active sorbent. The resistance to mass transfer for a sorbent of this type is reduced compared with the usual bulk phase sorbents, since the length of the diffusion path into the depth of the grain is reduced. Consequently, the duration of diffusion τ, which is now determined no longer by the grain diameter of the sorbent d but by the thickness of the active layer d_r, is also shortened. We shall estimate the shortening of the diffusion time assuming that $d = 0.3$ mm and $d_r = 0.05$ mm. In this case

$$\frac{\tau_{bulk}}{\tau_{surf}} \simeq \frac{d^2}{d_r^2} \simeq \frac{0.3^2}{0.05^2} \simeq 30.$$

Thus the use of surface layer sorbents should lead to an improvement of the efficiency of the chromatographic column.

In general sorbents with a surface-active layer may be called surface sorbents, in contrast to the usual bulk phase sorbents.

We believe it is desirable to classify surface sorbents on the basis of the characteristics of the active porous layer in accordance with the scheme in Fig. 1. The surface layer sorbents discussed here are divided into two types based on the type of the solid carrier employed, which can be either uniformly porous or can have a solid impermeable nucleus (for example, porous diatomaceous carriers or glass beads). Depending on the type of carrier, the methods of preparation and certain properties of sorbents of types I and II will differ.

Surface layer sorbents of type I (with an active porous layer on the surface of a solid nucleus) were first proposed by Halasz and Horvath[1] in 1962. Sorbents of type II were first obtained by Cremer in 1959, who introduced carbon black into the pores of Sterchamol to measure its specific surface[2] by the gas-chromatographic method. Granulated surface-porous sodium-borosilicate glasses were obtained by Zhdanov et al.[3] and etched ordinary glass beads were prepared by Ohline and Yoyola[4].

The possibility of using powdered adsorbents introduced into the pores of silica gels for gas-chromatographic analysis was first stated by Vasil'eva et al.[5] Surface layer sorbents of type II were first employed in gas-chromatographic analysis by Bombaugh[6] for the separation of air on molecular sieves deposited on Chromosorb and subsequently the method was employed by Keiser[7] to separate petrol fractions on graphitised carbon black deposited on Chromosorb.

A surface layer sorbent of type II was first obtained for gas-liquid chromatography by the authors of the review[8]. The use of surface layer sorbents gives rise to new possibilities in gas-chromatographic analysis and in the application of gas chromatography to the measurement of various physicochemical characteristics. This review deals with the methods of preparation of surface layer sorbents, the characteristics of the gas-chromatographic separation on them and their principal applications.

II. METHODS OF PREPARATION OF SURFACE LAYER SORBENTS

Surface layer sorbents can be used to achieve one of the familiar types of chromatography (gas–solid, gas–liquid, gas–liquid–solid, etc.)

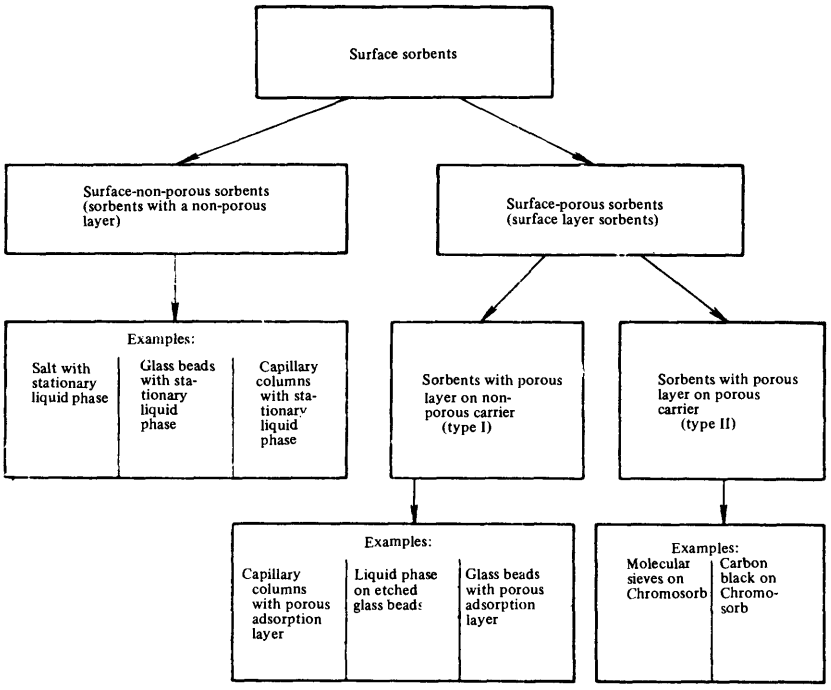

Figure 1. Scheme for the classification of surface sorbents in gas chromatography.

Halasz and Horvath[9] prepared sorbents of type I by precipitating a wide variety of adsorption materials from solutions on to the surface of non-porous glass or metallic beads, metallic spirals, and other carriers. The active sorbents employed were powdered alumina, aerosil, carbon black, or metal oxides with a stationary liquid phase [for example iron(III) oxide with polyesters]. It was found[9] that the particle size in the formation of a porous layer of metal oxides should be less than 0.1 μm. In order to obtain a more stable porous sorption layer, the glass beads were sometimes coated by a thin layer of varnish[9].

In gas–liquid chromatography a porous layer is obtained on beads using either glass microbeads (diameter 1 μm) or diatomaceous earth (diameter up to 10 μm), which are deposited together with the stationary liquid phase in a solvent. In this case the porous layer is retained on the beads by the surface tension forces of the liquid phase[10,11].

Another method for the preparation of sorbents of type I was described by Pope[12], who obtained an active porous layer on the surface of polyethylene beads on heating them to 160–170°C with graphitised carbon black. The polyethylene softens and the carbon black coats its surface.

Surface layer sorbents of type II are prepared using finely dispersed sorbents with a particle size up to 10 μm and solid coarsely porous carriers with a low specific surface: Chromosorb W, Chromosorb G, Celite-545. On mechanical shaking with solid carriers, finely dispersed adsorbents (molecular sieves, carbon black, activated charcoal, aerosil, etc.) enter into the macropores of the carriers and are retained there by adhesion forces, which determine the stability of the surface layer of the sorbent. Surface layer sorbents have been obtained in this way after prolonged mechanical shaking[6,7].

In order to determine the time required to obtain a surface layer sorbent, the variation of the amount of finely dispersed adsorbent deposited on the solid carrier with the duration of mechanical shaking was investigated[13]. This investigation was carried out on graphitised carbon black (particle size less than 1 μm) and Chromosorb W in proportions of 1 : 5. The amount of deposited carbon black was determined by elemental analysis for its carbon content. The deposition of the finely dispersed adsorbent (carbon black) in the pores of Chromosorb W terminates after 10–15 min (Fig. 2). Thus the duration of the preparation of the surface layer sorbent is as a rule short.

In the preparation of a surface layer sorbent of type II for gas-liquid chromatography, a stationary liquid phase is deposited in the usual way from a volatile solvent on a finely dispersed solid carrier with a particle size up to 10 μm, which may be obtained by sedimentation. Then the resulting finely dispersed sorbent is introduced into the macropores of an inert solid carrier by the mechanical shaking of the mixture for 10 mins.[14]

Chromosorb W or G modified by dichlorodimethylsilane or hexamethyldisilazane may be used as the inert solid carrier. Although these carriers are inert in relation to hydrocarbons and other non-polar compounds, it is recommended that for polar compounds the silylated Chromosorbs be additionally modified by a small amount (0.1%) of a polar liquid phase. Microscopic study of the distribution of the finely dispersed sorbent in the grains of a solid carrier showed that the small sorbed particles enter into the macropores of the solid carriers more or less uniformly over the entire "outer" surface, forming a surface layer to a depth of 20–50 μm with about 20% of the sorbent[13]. Another microscopic study[7] also showed that the active sorbent forms a surface layer, but its depth was

found to be 1–3 μm, the content of the active sorbent on the carrier being 5%. On surface layer sorbents of type I, the thickness of the surface layer varies between 1 and 100 μm.[9]

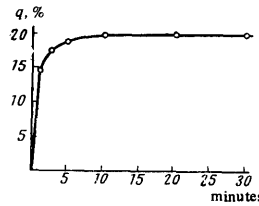

Figure 2. Variation of the amount of graphitised carbon black q deposited on Chromosorb W with time during mechanical shaking.

Thus a number of entirely satisfactory simple methods for the preparation of surface layer sorbents have now been developed.

III. CHARACTERISTICS OF GAS-CHROMATOGRAPHIC SEPARATION ON SURFACE LAYER SORBENTS

1. Retention Characteristics

In gas chromatography the retention values are some of the most important characteristics of the substance chromatographed. The retention on surface layer sorbents is in general due to the retention on the active sorbent and on the solid carrier. Therefore the reduced retention volume V_n for compounds chromatographed on surface layer sorbents can be represented by the following equation for gas-adsorption chromatography:

$$V_N = K_a S_a + K_c S_c \qquad (1)$$

or, for gas-liquid chromatography:

$$V_N = K_l V_l + K_c S_c \ , \qquad (2)$$

where K_a is the gas–active solid adsorbent partition coefficient, S_a the surface area of the absorbent in the column, K_c the gas–solid carrier partition coefficient, S_c the surface area of the solid carrier in the column, K_l the gas–stationary liquid phase partition coefficient, and V_l the amount of liquid phase in the column.

The above equations show that adsorption on a solid carrier can make a definite contribution to the retention volume (if necessary this contribution can be calculated from the equations). Therefore, in the preparation of surface layer sorbent it is desirable to employ inert solid carriers for which $K_c S_c \ll K_a S_a$ ($K_l V_l$).

Comparison of the relative retention times on sorbents of type I and bulk phase sorbents[9,15] revealed a small difference between the retention times.

With only a small contribution by adsorption on the solid carrier, the relative retention volumes of non-polar and weakly polar components on surface layer sorbents of type II correspond to the relative retention volumes on bulk phase sorbents (Table 1). This is the basis of the application of all the relations known for the identification of compounds chromatographed on bulk phase sorbents and the available tabulated relative retention values also to surface layer sorbents.

However, for polar compounds or for sorption-active carriers, such identification must involve an estimation of the contribution to the retention volume of the degree of adsorption of the substances chromatographed on the solid carrier.

Table 1. Relative retention volumes of hydrocarbons on bulk phase and surface layer sorbents of type II.

Substance analysed	Sorbent: squalane on Chromosorb W				Substance analysed	Sorbent: CaA molecular sieve	
	5% squalane		10% squalane				
	bulk phase	surface layer*	bulk phase	surface layer*		bulk phase	surface layer (CaA on Celite)
Benzene	0.18	0.19	0.18	0.18	Oxygen	0.31	0.32
Toluene	0.54	0.60	0.53	0.53	Nitrogen	1.00	1.00
n-Octane	1.00	1.00	1.00	1.00	Methane	1.81	1.75
n-Nonane	3.00	2.94	3.00	3.00	Carbon monoxide	5.30	5.60

*Surface layer sorbent: finely dispersed Chromosorb W with 5% (or 10%) of squalane deposited on Chromosorb W with a grain size of 0.4–0.25 mm.

2. Efficiency of Chromatographic Columns

The efficiency of chromatographic columns is characterised by the height equivalent to the theoretical plate (HETP), which is also determined by the type of sorbent used. Application of surface layer sorbents makes it possible to reduce HEPT, i.e. to increase the efficiency of the column compared with those containing bulk phase sorbents.

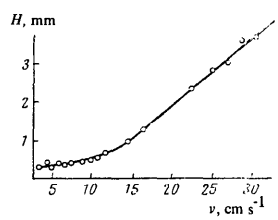

Figure 3. Variation of HETP (H) with carrier gas flow rate (v) for 3-chloropentane on a surface layer sorbent of type I. Experimental conditions: 100 × 0.2 cm column; temperature 90°C; carrier gas–nitrogen; flame ionisation detector.

In all studies dealing with surface layer sorbents of type I, a high efficiency of the columns filled with them was demonstrated. Thus Halasz and coworkers found that the minimum value of HETP on a column with glass beads and a porous adsorption layer is 0.4–0.5 mm.[16] In another study[15] the variation of HETP with the flow rate of the carrier gas for 3-chloropentane on a sorbent of this type is presented (Fig. 3). The data quoted show that HETP increases slightly as the flow rate rises to 15 cm s^{-1}, the minimum HETP being 0.38 mm. The efficiency of a column with polyethylene beads and graphitised carbon black was very high (HETP = 0.5–0.6 mm).[12]

Columns filled with glass beads on the surface of which diatomaceous earth with a stationary liquid phase had been

deposited are characterised by a minimum HETP = 0.8–1 mm.[10,11] It has been shown[4] that a column with etched glass beads (depth of pores 0.4 mm) has an efficiency higher than that of a column with unetched glass beads (Fig. 4).

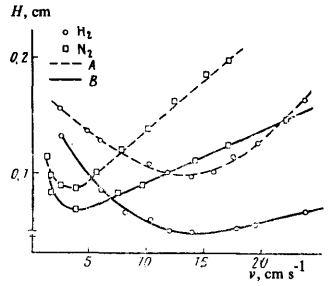

Figure 4. Variation of HETP (H) with carrier gas flow rate for n-nonane[5]: A) column with non-porous (unetched) glass beads; B) column with etched glass beads.

The efficiency of a column with a surface layer sorbent of type I has been compared with one containing a bulk phase sorbent only for porous glasses[3,17,18], and it was shown that the number of theoretical plates for the column with a surface-porous glass is higher by a factor of 2.6–7.5 compared with the column in which the glass is porous throughout the bulk phase, the duration of analysis of hydrocarbon gases being reduced by a factor of 8.

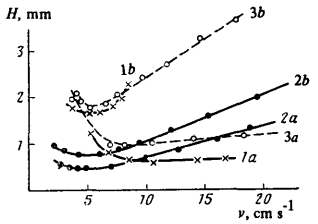

Figure 5. Variation of HETP (H) with carrier gas flow rate (v): 1) n-octane on graphitised carbon black; 2) toluene on Chromosorb W with 10% of squalane; 3) methane on CaA molecular sieves; a) surface layer sorbent; b) bulk phase sorbents.

The dependence of HETP on the mean linear flow rate of the carrier gas was investigated for columns with surface layer sorbents of type II and for the corresponding columns with bulk phase sorbents[14,19–21]. Typical relations between HETP and the carrier gas flow rate for gases on CaA molecular sieves deposited on Celite, for hydrocarbons on carbon black deposited on Chromosorb W, and for hydrocarbons on finely dispersed Chromosorb W on which squalane had been deposited are presented in Fig. 5.

The minimum HETP in these experiments on a column 4 mm in diameter was 0.45–0.50 mm (using a flame-ionisation detector) and 0.8–1.00 (using a katharometer).

A study of the dependence of HETP on flow rate established that, for columns with surface layer sorbents, (1) HETP is lower by a factor of 1.2–1.8 at the optimum carrier gas flow rate and by a factor of 1.7–3 in the range of higher flow rates compared with bulk phase sorbents, (2) the optimum carrier gas flow rate is high, particularly when surface layer sorbents are employed in gas-adsorption chromatography, and (3) the dependence of the efficiency on the rate is less pronounced than when bulk phase sorbents are employed.

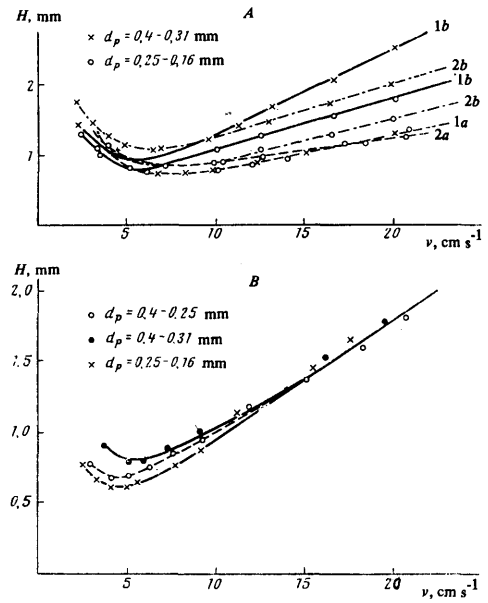

Figure 6. Variation of HETP (H) with carrier gas flow rate for n-octane (curves *1*) and toluene (curves *2*) on sorbents with different grain diameters. A): a) surface layer sorbent; b) bulk phase sorbent; detector–katharometer; carrier gas–helium; B) surface layer sorbent; n-octane; carrier gas–nitrogen; flame ionisation detector ("Khrom-2").

The effects of the grain diameter of the solid carrier on the chromatographic column efficiency has been investigated[14,19]. When surface layer sorbents of type II are used, a slight change in efficiency as a function of the carrier gas flow rate is observed for sorbents with different grain diameters only at low flow rates, while at high flow rates, where the spreading is determined by the mass-exchange kinetics, the difference in efficiency becomes smoothed out. The efficiency of columns with bulk phase sorbents measured under the same conditions decreases with the grain diameter (Fig. 6). The reason for this is that not the entire grain but only the surface layer, whose thickness is determined by the depth of the solid carrier pores and does not therefore change with the grain diameter, is involved in the mass-exchange process.

Consequently, with surface layer sorbents of type II, one can use fairly large solid carrier grains, which has

little effect on column efficiency but reduces the resistance to the carrier gas flow and makes it possible to operate at higher flow rates and with longer columns for low pressure differences.

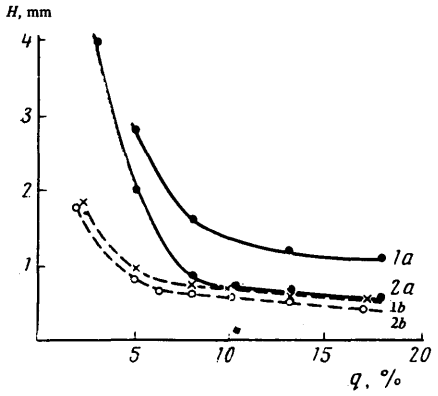

Figure 7. Variation of HETP (H) for toluene (curves *1*) and n-octane (curves *2*) on surface layer sorbents with the content of the active sorbent (g): *a*) column with graphitised carbon black on Chromosorb W; *b*) Chromosorb W with finely dispersed Chromosorb W on which 10% of squalane had been deposited.

The study of the effect on column efficiency of the amount of the active sorbent deposited on the solid carrier showed that, with increase of its content up to 8–10%, the efficiency increases rapidly and then changes only slightly (Fig. 7).

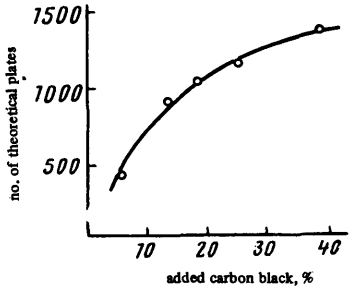

Figure 8. Variation of a number of theoretical plates for n-hexane with the content of carbon black on polyethylene beads[17].

An analogous effect of the amount of active sorbent on the efficiency of the column with a surface layer sorbent of type I was demonstrated in a study[12] where the variation of the number of theoretical plates with the amount of carbon black deposited on polyethylene beads was investigated (Fig. 8). The relation shows that, for low carbon black contents, the number of theoretical plates increases rapidly and then significantly more slowly, starting with about 20% of the black. Thus the dependence of HETP on the amount of active sorbent for surface layer sorbents is of the same type as the dependence of the coefficient of resistance to mass transfer (in the HETP equation for the usual sorbents) on the extraction coefficient[22].

In a study of the efficiency of columns with surface layer sorbents, it is interesting to estimate the contributions of various processes to the spreading of chromatographic zones. For this purpose, it is useful to employ the Giddings equation[23], which agrees well with the experimental data:

$$H = \frac{1}{1/A + 1/c_m v} + \frac{B}{v} + cv \cdot \qquad (3)$$

Here the first term describes the coupled eddy diffusion, the second the molecular longitudinal diffusion, and the third the mass exchange kinetics.

The coefficients of the Giddings equation, determined from the experimental $H = H(v)$ relations by a graphical method[24] for surface layer sorbents of type II and the corresponding bulk phase sorbents in gas-adsorption and gas liquid chromatography, are presented in Table 2, which shows that, when surface layer and bulk phase sorbents are employed, systematic relations between the coefficients of the HETP equation are observed mainly for the coefficient of resistance to mass transfer C, which is lower for surface layer sorbents by a factor of 3–4 in gas-adsorption chromatography and by a factor of 1.8 in gas-liquid chromatography.

Table 2. The coefficients in the Giddings equation for bulk phase and surface layer sorbents of type II.

Sorbent	Compound chromatographed	Expt. conditions: column length, m	Expt. conditions: temp., °C	A, cm	B_2, cm s^{-1}	C_m, s	C, s
Molecular sieve, bulk phase sorbent	methane	1	20	0.080	0.37	0.0120	0.0160
Molecular sieve on Celite, surface layer sorbent	methane	1	20	0.060	0.60	0.0020	0.0038
Aerosilogel, bulk phase sorbent	n-decane	1	120	0.070	0.78	0.0010	0.0173
Aerosilogel on Chromosorb, surface layer sorbent	n-decane	1	120	0.060	0.55	0.0020	0.0053
Carbon on Chromosorb, surface layer sorbent	n-hexane	1	80	0.014	0.12	0.0006	0.0050
Chromosorb W with 5% of squalane, bulk phase sorbent	n-octane	0,8	60	0.020	0,15	0.0020	0.0110
Chromosorb W with 5% of squalane, surface layer sorbent	n-octane	0,8	30	0.024	0.10	0.0030	0.0061

Table 2 lists the overall coefficients C in the Giddings equation reflecting the resistance to mass transfer, which includes the resistance to mass transfer in the gas (mobile) and stationary phases. In the determination of the separate contributions to mass exchange, the Perrett–Purnell method, based on the measurement of the coefficient C for two carrier gases of different types[25], was employed. The separate determination of these contributions has been made for methane on the CaA molecular sieve and for n-octane on Chromosorb W with 10% of squalane. The results are presented in Table 3, which shows that the resistance to mass transfer in the gas phase is lower by a factor of 10 for methane on the molecular sieves and by a factor of 1.7 for n-octane in gas-liquid chromatography. The explanation is that the mass exchange in the gas phase for surface layer sorbents

of type II does not depend on the grain diameter but on the thickness of the layer of the active sorbent which amounts to 20–50 μm according to microscopic measurements, i.e. is much smaller than the grain diameter. Consequently the diffusion path traversed by molecules into the bulk of the grain is shortened, since the active sorbent is located in the surface layer in the immediate vicinity of the gas stream, which accelerates the mass exchange and permits analysis at higher rates, i.e. the duration of analysis is reduced.

Table 3. Coefficients of resistance to mass transfer in gas at stationary (liquid) phases.

Type of Chromatography	Sorbent	Compound chromatographed	Resistance to mass transfer	
			gas phase	stationary phase
Gas-adsorption	CaA on Celite (surface layer sorbent)	methane	0.0002	0.0036
	CaA, bulk phase sorbent	methane	0.0020	0.0140
Gas-liquid	Chromosorb W with 10% of squalane, surface layer sorbent	n-octane	0.0013	0.0022
	Chromosorb W with 10% of squalane, bulk phase sorbent	n-octane	0.0022	0.0029

The increase of the mass transfer coefficient explains the lower minimum HETP, the less pronounced dependence of HETP on the rate, and hence the considerable decrease of HETP at high carrier gas flow rates for surface layer sorbents; hence, these sorbents are useful for rapid analysis.

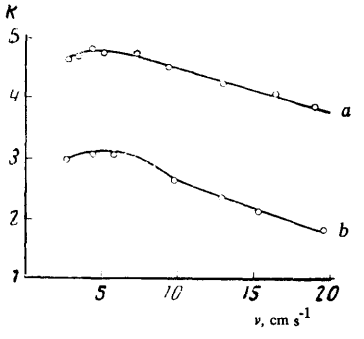

Figure 9. Variation of the separation factor K_1 (toluene–octane) with carrier gas flow rate (v) for surface layer (a) and bulk phase (b) sorbents.

3. The Separation Factor

The real improvement of separation is determined not only by the number of theoretical plates but also by the separation factor, which is one of the principal characteristics determining the usefulness of various sorbents in gas chromatography. The separation factor K_1 is defined by the following equation[26]:

$$K_1 = \frac{\sqrt{2}}{4} K_s \sqrt{N} \quad , \qquad (4)$$

where K_S is the selectivity coefficient and N the number of theoretical plates.

In studies on surface layer sorbents of type I, the separation factor was not as a rule considered as a characteristic of columns with the sorbent. Only in experiments with surface-porous glasses was it shown that the separation factor for hydrocarbon gases is higher by a factor of 1.3 compared with glasses porous throughout their bulk[3].

An experimental comparison of the separation factors for the toluene–octane pair on surface layer sorbents of type II and bulk phase sorbents has been made[14] under the conditions of a constant duration of analysis. Fig. 9 presents the relations between the separation factor and the rate under these conditions. In all cases the separation factor was higher for the surface layer sorbent by a factor of 1.2–1.5 compared with the bulk phase sorbent.

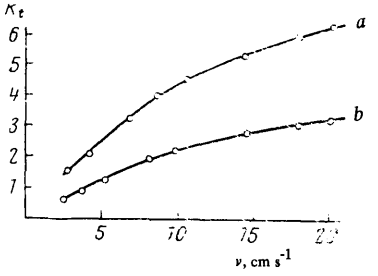

Figure 10. Variation of K_t with the carrier gas flow rate on CaA molecular sieves: a) surface layer sorbent; b) bulk phase sorbent.

Under other comparison conditions (for example, for the same volumes of the sorbent), the time characteristic of the separation factor (K_t) can be usefully employed for the estimation of the separating capacity of surface layer and bulk phase sorbents:

$$K_t = K_1 / t_R \quad , \qquad (5)$$

where K_1 is the separation factor and t_R are the mean elution times of the components for two adjacent peaks.

The separating capacity of columns with molecular sieves in the surface layer and bulk phase versions was estimated by the present authors in terms of the relation between K_t for the nitrogen–methane pair and the flow rate (Fig. 10). Fig. 10 shows that the use of the CaA molecular sieve on Celite as a surface layer sorbent shortens the duration of separation of the gases by a factor of 3 for the same separation factor compared with the bulk phase sorbent. The reduction of the duration of analysis is undoubtedly a valuable advantage of surface layer sorbents.

Thus surface layer sorbents are usually characterised by a higher separation factor and a shorter duration of analysis compared with bulk phase sorbents; they can be used at lower temperatures, which extends the range of compounds susceptible to analysis.

IV. ANALYTICAL APPLICATIONS OF SURFACE LAYER SORBENTS

Surface layer sorbents can be used in the separation of various specific systems in all known versions of gas chromatography. As already mentioned above, the

Table 4. Examples of the applications of surface layer sorbents for the separation of mixtures.

Mixture analysed	Sorbent characteristic	Duration of analysis, min	Conditions of analysis				Refs.
			column length, cm	temp., °C	carrier gas flow rate	detector*	
I. Gas mixtures							
H_2; O_2; N_2; CH_4; CO	CaA molecular sieves on Celite-545 (20 wt.%)	0.2	100×0.4	20	50 cm s^{-1}	K	19, 20
CH_4; C_2H_6; C_2H_4	Surface-porous glass	3	100×0.4	40	7 cm s^{-1}		3
C_3H_8; C_3H_6	Glass porous throughout bulk	24	100×0.4	40	7 cm s^{-1}		3
C_1–C_4 hydrocarbon gases	NaX molecular sieves on Celite-545 (20 wt.%)	18	100×0.3	30—160		FID	19, 20
II. Hydrocarbons							
C_{15}–C_{35} n-alkanes	90% glass beads, 9% iron(III) oxide, 0.9% Carbowax 4000 (monostearate), 0.1% potassium hydroxide	11	200×0.2	190	progr. pressure	FID	27
C_9–C_{16} n-alkanes	Aerosil on Chromosorb G (5 wt.%)	6.5	80×0.4	150	50 ml min^{-1}	FID	21
	Aerosil, bulk phase sorbent	52	80×0.4	150	50 ml min^{-1}	FID	21
C_9–C_{26} n-alkanes	Aerosil on Chromosorb G (5 wt.%)	15	100×0.3	120—300		FID	21
C_6–C_{13} n-alkanes	Graphitised carbon black on Chromosorb R (5 wt.%)	5.5	400×0.2	30—350		FID	7
Aromatic hydrocarbons: trimethylbenzenes, tetrahydronaphthalene, methylnaphthalenes	90% of glass beads, 9% of iron(III) oxide, 0.9% Carbowax 4000, 0.1% of potassium hydroxide		200×0.2	190		FID	15
Terphenyls	Graphitised carbon black on Chromosorb W (20 wt.%)	4	20×0.4	290	10 cm s^{-1}	FID	13
	Granulated graphitised carbon black (bulk phase sorbent)	5.5	20×0.2	360	30 ml min^{-1}	FID	28
cis- and *trans*-Decalins	Graphitised carbon black on Chromosorb W (20 wt.%)	2	100×0.3	120	10 cm s^{-1}	FID	13
	Granulated graphitised carbon black (bulk phase sorbent)	6	200×0.3	210	50 ml min^{-1}	FID	29, 30
α-, and β-isopropylnaphthalenes	Graphitised carbon black on Chromosorb W (20 wt.%)	6	100×0.3	240	12 cm s^{-1}	FID	13
Propyltoluene and xylenes	Finely dispersed Chromosorb impregnated with 15% of a mixture of DS-550 silicone oil and Bentone-245 (60:40) on Chromosorb (16 wt.%)	10	200×0.3	45	60 ml min^{-1}	FID	14
C_9–C_{12} cyclic hydrocarbons	Ditto	11	200×0.3	80—100		FID	14
III. Oxygen-containing and other compounds							
Terpenes	90% of glass beads, 9% of iron(III) oxide, 0.9% of Carbowax 4000, 0.1% of potassium hydroxide	0.5		180	16 cm s^{-1}	FID	15
ethyl esters of aliphatic acids	Finely dispersed Spherochrome-1** with 7% PEGA*** on Chromosorb G	6.5	200×0.4	175	120 ml min^{-1}	K	14
	Spherochrome-1** with 12% PEGA*** (bulk phase sorbent)	34	200×0.4	200	120	K	31
Methyl esters of C_8–C_{19} aliphatic acids	93% of glass beads, 6.3% of iron(III) oxide, 0.7% of versamide	3	200×0.2	245	progr. pressure	FID	27
C_1–C_8 n-alcohols	Graphitised carbon black on porous Teflon	8	100×0.3	60—200		FID	32
Cyclohexylchlorobenzenes	Graphitised carbon black on Chromosorb W (20 wt.%)	5	100×0.3	210	14 cm s^{-1}	FID	
Butylphenols, phenol, 2,6-dibutylphenol, *o*-butylphenol, *p*-butylphenol, 2,4-dibutylphenol	Finely dispersed Chromosorb W with 2% of neopentylglycol succinate deposited on Chromosorb G	5.5	100×0.3	100—150	12 cm s^{-1}	FID	13

Table 4 Cont'd.

Mixture analysed	Sorbent characteristics	Duration of analysis, min	Conditions of analysis				Refs.
			column length, cm	temp., °C	carrier gas flow rate	detector*	
Cresols (*ortho-*, *meta-*, *para-*)	Finely dispersed Chromosorb W with 6% of a mixture of pentaphenyl ether**** and bentone-245 (1 : 1) deposited on Chromosorb (15 wt.%)	8	200×0.3	110	7	FID	13
Nitrotoluenes (*ortho-*, *meta-*, *para-*)	Finely dispersed Spherochrome-1 with 7% PEGA on Chromosorb G (15 wt.%)	7	200×0.4	140	6	K	13

*K = katharometer; FID = flame-ionisation detector (Translator).

**Possibly a Russian name—Sferokhrom-1 (Ed. of Translation).

***Probably poly(ethylene glycol adipate) (Ed. of Translation).

****Probably pentyl phenyl ether (Ed. of Translation).

employment of surface layer sorbents has many advantages in the separation of mixtures compared with the usual sorbents. In addition they are characterised by fairly high mechanical strength. This permits the use of programmed temperatures and pressures. Table 4 presents examples of the practical applications of surface layer sorbents for the separation of various classes of compounds. In some cases the compounds were analysed for comparison on bulk phase sorbents.

V. APPLICATIONS OF SURFACE LAYER SORBENTS IN PHYSICOCHEMICAL STUDIES

Surface layer sorbents of type II can be used not only for analytical purposes but also for the measurement of physicochemical characteristics by gas chromatography.

As already stated, a surface layer sorbent of type II was first employed by Cremer[2] to determine the specific surface of carbon black introduced into the pores of Sterchamol, i.e. the first application of the surface layer sorbent in gas chromatography was its employment for physicochemical studies. Indeed, in the investigation of highly dispersed adsorbents by the chromatographic method, when they are used directly to fill the chromatographic column, it is necessary to employ very high pressures in order to achieve the required flow rate of the carrier gas. Therefore, as a rule granules and not the initial powder are employed as packing. The granules are obtained by pressing the powders or by using a binder, but the introduction of the latter into the sorbent composition in general alters its properties. Therefore we believe it simpler, more universal, and more convenient to investigate disperse adsorbents introduced into the pores of solid carriers rather than use specially prepared granules. It is noteworthy that, in the preparation of a column of the same length, a smaller amount of adsorbent is required, which is important in the study of new adsorbents.

Kiselev and coworkers employed a surface layer sorbent of type II to investigate the retention volumes and heats of adsorption of hydrocarbons on graphitised[33] and acetylene carbon blacks[34] and also to determine the specific surfaces of the blacks. A macroporous silica gel with a specific surface of 9 $m^2 g^{-1}$ was used as a solid carrier.

According to Eqn. (1), the interpretation of the chromatographic results is simplest and most accurate when the contribution of the solid carrier to the retention volume is low. Therefore one may recommend as solid carriers macroporous materials with a low specific surface (significantly lower than the specific surface of the disperse adsorbent) on which there is virtually no adsorption of the components investigated. The use of surface layer sorbents has many advantages even in those cases where the preparation of granulated material presents no difficulties. The two methods were compared in the determination of the heats of adsorption of straight-chain alkanes on a surface layer sorbent: NaX molecular sieve[35]. The heats of adsorption obtained with various types of sorbent are virtually identical. In this paper it is also noted that the use of a surface layer sorbent leads to the following possibilities compared with the bulk phase sorbents: (1) the amount of adsorbent may be reduced and very finely dispersed powder may be employed for measurement; (2) the experimental temperature may be lowered (on average by 100 deg); (3) the range of compounds investigated may be extended using higher-boiling substances; (4) measurements may be made under conditions closer to equilibrium owing to the acceleration of mass transfer. It is noteworthy that surface layer sorbents can also be used for the measurement of other characteristics, in particular in the study of kinetics under pulse conditions.

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In conclusion we may note that the advantages discovered in many fields of gas chromatography when surface layer sorbents are used and their successful applications permit their recommendation for large-scale employment in chromatographic practice.

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Rare-earth Fluorides

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The methods of preparation of simple and double rare-earth fluorides both in the normal, tervalent state and in bivalent and quadrivalent states have been examined. The structures of these compounds, their polymorphic modifications, and the characteristics of the formation of solid solutions are discussed.
The physicochemical properties of fluorine-containing rare-earth compounds have been compared with the type of chemical bonding and the characteristics of the electronic structure of rare-earth atoms. Data are presented on the behaviour of rare-earth fluorides in systems containing the fluorides and oxides of other elements.
The bibliography includes 372 references.

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I. INTRODUCTION

In recent years there has been a considerable growth of interest in the study of rare-earth fluorides owing to the development of new applications of rare-earth trifluorides and their compounds with the fluorides of other elements, for example in laser engineering and microelectronics. This requires not only an improvement in the methods of preparation and purification of the fluorides but also the development of ways of growing optical single crystals, refinement of data on their structure, and the elucidation of the structural characteristics of activated fluorides.

An important field of application of rare-earth fluorides is also metallurgy, since in metal thermite reduction the most suitable materials for the preparation of pure metals are in fact the trifluorides [1-5].

The trifluorides are also important in nuclear engineering, analytical chemistry, and the technology of the separation of elements, where use is made of the low solubility of rare-earth trifluorides in water and acids for the separation of the rare earths and isolation of transuranic elements with LaF_3 as a carrier. The comparatively low volatility of the trifluorides at high temperatures constitutes the basis of their application in the separation of uranium as UF_6 from fission products in the course of the regeneration and purification of nuclear fuel [6-8]. Thus knowledge of the chemical and structural characteristics of rare-earth fluorides, of the characteristics of their interaction with the fluorides and other metals, and in general of their behaviour in various systems is important for many branches of modern engineering.

Reviews on rare-earth fluorides deal mainly with an earlier period [9-11] or are concerned only with certain properties of the trifluorides [12], the methods of their synthesis [13,14], or the laser properties of the fluorides [15-17]. Of the publications in recent years, mention may be made

of Toma's review[18] and Brown's monograph[19] on lanthanide and actinide halides.

This review surveys the available information on the chemical and physicochemical properties of rare-earth trifluorides, their compounds with alkali metal and alkaline earth metal fluorides, and rare-earth oxide fluorides and fluorides in which the valence of the rare earth is other than 3. Much attention has been devoted to the structural and crystal-chemical characteristics of these compounds, since they determine many properties important in practice. The problems associated with the laser characteristics of activated fluoride crystals are not discussed, since they are frequently dealt with in the literature, including the chemical literature[15-17].

In this review the rare-earth elements include lanthanides and yttrium.

II. SYNTHESIS AND PROPERTIES OF RARE-EARTH TRIFLUORIDES

1. Preparation of Anhydrous Rare-earth Trifluorides

Anhydrous rare-earth trifluorides are prepared by methods involving the dehydration of products precipitated from solutions of the salts of these elements with hydrofluoric acid or synthesised by fluorinating rare-earth oxides.

1. Hydrofluoric acid precipitates from aqueous rare-earth salt solutions trifluorides containing a certain amount of water[20,21], which depends considerably on the conditions of their precipitation and washing[23-25]. Lanthanum trifluoride almost free from water can be obtained from a solution of the nitrate in 95% ethanol[22].

Hydrated trifluorides lose weight at a temperature as low as 40–60°C,[23,24] but they cannot be dehydrated by heating in air, since water is not completely removed at a low temperature (up to 300°C) and at a higher temperature the trifluorides are partly hydrolysed with formation of oxide fluorides. According to Wendlandt and Lowe[23], most of the water-containing trifluorides lose weight continuously on heating in air from 40° to 900°C and only a few of them (NdF_3, GdF_3) may be obtained by dehydration (350–375°C) without an appreciable contamination by oxide fluorides. The precipitates dried at 100–150°C still contain several per cent of water[26].

In order to prepare the anhydrous trifluorides, the hydrated products subjected to an initial heat treatment at 100–150°C are heated in a vacuum at 300–350°C[2,3,27] or in a stream of hydrogen fluoride and an inert gas[1,2,5,28,29] at 600–1000°C. Sometimes anhydrous trifluorides are prepared by treating their hydrates with an excess of NH_4F or NH_4HF_2, the volatile products being subsequently distilled off[13,30,31].

Heat treatment of hydrated trifluorides enriched in ^{18}O isotope in an inert atmosphere and mass-spectrometric determination of oxygen in the heat-treatment products lead to the conclusion that dehydration terminates at about 500°C without an appreciable formation of oxide fluorides and oxides[32]. However, according to other data[33], the gas phase over lanthanum trifluoride during dehydration in an atmosphere of argon contains a small amount of HF even at 500°C, which must indicate the hydrolysis of LaF_3.

The oxygen content in the trifluorides obtained by dehydration at 300°C and 10^{-2} mmHg usually does not exceed 0.02%.[27,33] However, in many cases the content is higher (up to 0.06%)[5,34]. Probably the powdered trifluorides are contaminated also due to the adsorption of moisture and oxygen from air[1,32]. Therefore it is best to store the trifluorides in a re-melted form or after heat treatment in an inert atmosphere at a temperature close to the melting point of the trifluoride[27,33]. Cryptocrystalline powders which have been stored for a long time must be reheated in a stream of anhydrous hydrogen fluoride or an inert gas.

The trifluorides are precipitated with hydrofluoric acid from salt solutions in plastic (Teflon, polyethylene) or platinum vessels. The precipitation, filtration, and washing operations involving large amounts of precipitates (up to 45 kg) may be performed using special apparatus consisting of reactors with mechanical stirrers and plastic filters[5].

The hydrated trifluoride precipitates are obtained in a finely dispersed form and are therefore difficult to filter. Prolonged filtration may be omitted sometimes by using instead centrifugation and decantation with subsequent drying of the precipitate under an infrared heater or on a water bath[35].

Several methods have been proposed for the preparation of trifluorides in a better crystalline state. One of these consists in treating with hydrofluoric acid a suspension of the rare-earth hydroxide in water[36]. The hydrated precipitates obtained in this way are filtered more readily and contain less impurities. A similar result is obtained when a suspension of the rare-earth carbonate is employed[37]. Readily filtered fluorides can also be prepared by precipitation from chloride solutions at 100°C with liquid anhydrous hydrogen fluoride[5]. Terbium trifluoride is prepared by saturating a solution of the chloride in absolute alcohol with hydrogen fluoride. The oxygen content in the metal obtained from this fluoride was only 0.01%.[38]

2. Methods involving the fluorination of rare-earth oxides are best for the preparation of the anhydrous trifluorides. Gaseous fluorine and hydrogen fluoride or the solid fluorides NH_4HF_2 and NH_4F may be used as fluorinating agents. Gaseous fluorine is rarely employed[39] and the hydrofluorination procedure and the method based on the reaction with ammonium hydrogen fluoride have acquired practical importance. Both methods lead to a good yield and a fairly pure product. Under laboratory conditions, the method involving the fluorination of Ln_2O_3† with ammonium hydrogen fluoride is more widely employed, being simpler and more readily available.

The reaction of rare-earth oxides with anhydrous HF yielded all the rare-earth fluorides[5,29,40,41]. The optimum hydrofluorination temperature is apparently 700°C and its duration ranges from 2 hours upwards, depending on the amount of oxide. In the preparation of the trifluorides in amounts up to 1 kg in 99.8–99.9% yield, Carlson and Schmidt[5] used fluorination with anhydrous HF in a stationary oxide bed. In order to remove the hydrogen fluoride adsorbed by the trifluoride, the reaction products must be cooled in a stream of inert gas.

Direct hydrofluorination in a stationary furnace does not go to completion when the amount of oxide in the charge is increased to tens of kilograms. Fluorination with a rotating oxide bed increases the yield of the trifluoride[42]. The use of a rotating bed prevents the formation of a fluoride crust on the surface of the oxide which interferes with diffusion into its deeper layers. One of the possible

† In this formula and subsequently, Ln denotes a rare-earth element.

types of apparatus with a rotating bed has been described by Carlson and Schmidt[5].

The rate of reaction of Ln_2O_3 with HF and the yield of trifluoride can also be enhanced by fluorination in a fluidised bed. This method has been used to prepare yttrium trifluoride[43]. A reactor for fluorination in a fluidised bed, suitable for the simultaneous treatment of 0.9–1.8 kg of the oxide, is described in the review of Carlson and Schmidt[5]. In this reactor a fluidised bed is produced by a stream of nitrogen, which is replaced by hydrogen fluoride when the temperature in the fluidised bed reaches 150°C. The fluorination of the above amounts of Y_2O_3 at 600–700°C goes to completion in 7–10 h.

The possibility of employing chlorine trifluoride as a fluorinating agent has been investigated[44]. The degree of fluorination of lanthanide oxides by ClF_3 is unequal for different elements of the series and decreases with the atomic number of the element. The fluorination process takes place quantitatively only for the oxides of the lighter elements which have been subjected to a preliminary hydration.

Metallic yttrium, lanthanum, and cerium react with liquid hydrogen fluoride at 150–250°C, forming anhydrous trifluorides[45].

The reaction of rare-earth oxides with NH_4HF_2 and NH_4F. Rare-earth trifluorides can be obtained by treating the oxides with an excess of ammonium hydrogen fluoride or fluoride at 200°C and subsequent removal of the reagent in a stream of an inert gas at 450–600°C.[1,5,46,47] Spedding and Daane[1] obtained in this way the trifluorides of all the rare earths in amounts of up to 1 kg. In order to prepare pure products by fluorination with ammonium hydrogen fluoride or NH_4F, repeated treatment with the reagent is recommended[47]. Although the main bulk of ammonium fluoride sublimes at 300°C, its final removal requires a higher temperature (up to 600°C). The heat treatment must be carried out in a stream of a carefully dried inert gas in order to prevent the hydrolysis of the trifluoride. If the trifluoride obtained is used for reduction to the metal, particular attention must be paid to the complete removal of ammonia in order to avoid the contamination of the metal with nitrogen.

When rare-earth oxides are treated with ammonium hydrogen fluoride or fluoride (200–250°C), double fluorides of the rare earth and ammonium are formed as intermediates, decomposing on heating above 300°C. In addition, double fluorides can be obtained as a result of a double decomposition reaction in the aqueous solution between the rare-earth salts and an excess of ammonium fluoride and can be used to prepare the anhydrous trifluorides[48–51]. For this purpose, they are subjected to thermal decomposition in a stream of a dry inert gas. In this case too the complete removal of NH_4F is achieved on heating to 600°C. A double ammonium rare-earth fluoride obtained by precipitation from aqueous salt solutions with an excess of NH_4F and dried in air can be usefully treated with a large amount of ammonium fluoride, which is then distilled off in a stream of argon or helium[51]. This procedure creates better conditions for the prevention of the pyrohydrolysis of the fluorides.

The trifluorides obtained by the reaction of the oxides with ammonium hydrogen fluoride or by the thermal decomposition of the double compounds of the rare earths and ammonium are quite suitable for use as starting materials in the growing of optical crystals[52,53], but one should remember that on storage they adsorb gases and moisture from air.

The reaction of rare-earth nitrates and alkali metal and ammonium fluorides in a melt of $KNO_3(NaNO_3)$ and NH_4NO_3. Potassium (or sodium) fluoride precipitates anhydrous rare-earth trifluorides from melts of rare-earth nitrates in $KNO_3(NaNO_3)$[54,55]. The precipitation must be carried out with a stoichiometric amount of the reagent, since in the presence of its excess the trifluorides formed initially are converted into double fluorides. The precipitates may be separated from the nitrate by washing with water and decantation.

Ammonium fluoride can also be used as a precipitant for rare-earth ions in an ammonium nitrate melt. In this case it is recommended that the precipitation be carried out with an excess of NH_4F and subsequent distillation of volatile products in a vacuum at 450°C[54].

Precipitation from nitrate melts yields the anhydrous trifluorides of the majority of the rare earths in the form of larger crystals, compared with, for example, the thermal decomposition of the double compounds with ammonium fluoride.

Preparation of optical crystals of the trifluorides. Rare-earth trifluorides have excellent optical properties, are readily alloyed with rare-earth activators, and constitute an excellent base for lasers and photon counters. In this connection the growing of optical trifluoride crystals is a problem of practical importance.

Methods involving crystallisation of the melts are used to prepare optical rare-earth trifluoride single crystals. A necessary condition in the growing of single crystals is the prevention of the pyrohydrolysis of the trifluorides, which leads to the formation of oxygen compounds: even insignificant admixtures of the latter cause a turbidity in the crystal. The single crystals are best synthesised in a fluorinating atmosphere[56,57] but optical single crystals can also be obtained in an inert atmosphere[53,58]. In this method the starting materials must be very carefully freed from oxides and oxide fluorides, while in a fluorinating atmosphere these are converted into the fluorides. The preliminary purification of the starting material consists usually in its hydrofluorination with anhydrous hydrogen fluoride at 700–800°C.[56,58] The necessity for careful drying of the inert gas and hydrogen fluorides must also be emphasised, since the trifluorides are readily hydrolysed at 1400–1500°C even at a negligibly low water vapour pressure[59]. The fluorinating agents which can be employed are fluorine, hydrogen fluoride, and also the fluorides of certain elements, for example PbF_2 and CdF_2,[57,60,61] which are introduced into the charge before fusion, and their oxides as well as the fluorides themselves are evaporated during the fusion process. As in the growing of alkaline earth metal fluoride crystals, a fluorinating atmosphere may be produced from Teflon[62,63], the thermal decomposition products of which react not only with oxides but also with water, forming hydrogen fluoride[63].

The single crystals are grown in graphite or platinum crucibles. Account must be taken of the reducing properties of these materials in relation to certain fluorides, particularly those of europium and samarium[61,64,65], which are apparently promoted by admixtures of certain oxygen compounds[59]. Thus in the growing of lanthanum trifluoride crystals with added SmF_3 and EuF_3 in an inert or a weakly fluorinating atmosphere, partial reduction of the samarium and europium salts takes place, whereas in a strongly fluorinating atmosphere such reduction is not observed[61,64].

Optically homogeneous single crystals of the trifluorides are obtained by Stockbarger's method. All the trifluorides in the hexagonal modification (LaF_3, CeF_3, PrF_3, and NdF_3)[53,56,57,66,67], pure or activated with rare-earth elements, have been obtained by this method or its somewhat modified version. Lanthanum and cerium trifluorides, which are transparent over a wide spectral range, are of great interest as optical materials. Optical crystals with a mixed composition of the type $(La_xNd_{1-x})F_3$ $(0 \leq x \leq 0.5)$ have been obtained from hexagonal fluorides[57]. Good optical crystals of lanthanum trifluoride containing the fluorides of heavier elements, which crystallise in the orthorhombic system, can be obtained only when the content of the latter is low.

Czochralski's method has also been successfully used to prepare single crystals of the hexagonal trifluorides[58,68].

The synthesis of perfect crystals of the orthorhombic trifluorides is complicated by the occurrence of the polymorphic transformation $LnF_3(rhomb.) \rightleftharpoons LnF_3(hex.)$. Only two of these ($DyF_3$, HoF_3), the temperatures of the polymorphic transformations of which are close to the melting points, have been obtained in the form of single crystals with dimensions of several centimetres[57].

2. The Structure of Rare-earth Trifluorides

Rare-earth trifluorides crystallise in the hexagonal or orthorhombic system. Only the hexagonal modification, with a tysonite type structure, is known for lanthanum, cerium, praseodymium, and neodymium trifluorides[69,70]. The orthorhombic modification (YF_3 structural type) is characteristic of the trifluorides of the heavier elements under the usual conditions[29]. A cubic modification of YF_3 has been reported[71], but subsequently it was found[29] that these results did not refer to yttrium trifluoride itself but to its compound with sodium fluoride. Above 555–1100°C, the orthorhombic trifluorides undergo a structural change and are converted into the hexagonal modifications. According to the data of Toma and Brunton[72], the high-temperature forms of the trifluorides of the elements ranging from samarium to holmium have tysonite type structures and can be obtained in a metastable state below the polymorphic transition temperature by means of quenching. The hexagonal modifications of erbium, ytterbium, lutetium, and yttrium trifluorides differ from the tysonite type. Below the phase transition temperature, they are unstable.

Table 1 lists the dimensions of the unit cells of the hexagonal and orthorhombic modifications of LnF_3 and the polymorphic transition temperatures $[LnF_3(rhomb.) \rightleftharpoons LnF_3(hex.)]$.

The first X-ray diffraction studies on tysonite type trifluorides were made by Oftedal[69], who established that the structure of this type has a hexagonal unit cell with the space group $C6_3/mcm(D^3_{6h})$. The subsequent revision of atomic coordinates[74,75] led to the conclusion that the positions of lanthanum atoms in the LaF_3 structure virtually correspond to the model with the space group $C6_3/mcm$, while fluorine atoms are displaced compared with the positions expected for this model; therefore lanthanum trifluoride crystals can be more correctly assigned to the trigonal system (space group $P\bar{3}c1$). The coordination sphere about lanthanum is formed by 9 fluorine atoms at a distance of 2.4–2.6 Å from the metal and two more remote atoms at a distance of 3.0 Å.

A somewhat different structural model was suggested for LaF_3 by Rango and Tsoucaris[76]. This model corresponds to the space group $P6_3cm$. In general the differences between the models are small and the real LaF_3 structure differs little from the ideal case (space group $C6_3/mcm$).

To elucidate the structural characteristics of the hexagonal trifluorides, other methods, particularly NMR, were used together with X-ray diffraction analysis. The ^{19}F NMR spectrum confirms the presence in the trifluoride structures of non-equivalent fluorine atoms and of a unit cell with 6 formula units[77–80]. Analysis of the ^{139}La and ^{19}F NMR spectra of an LaF_3 single crystal together with certain X-ray diffraction data leads to the conclusion that the crystals have hexagonal symmetry (space group $P6_3/cm$), but, according to the authors themselves[78], this result can be explained by the twinning of crystals with trigonal symmetry. At the same time ^{19}F NMR data for CeF_3 were found to agree well with the space group $P\bar{3}c1$.[80] One of the reasons for the discrepancies in the data on the symmetry of crystals belonging to the tysonite structural type may be a disordered distribution of fluorine atoms among all possible sites. The diffusion-dependent narrowing of the lines at room temperature, which is characteristic of ^{19}F NMR spectra, should be noted in this connection[77,81–83]. The observed mobility of fluorine atoms at a relatively low temperature can evidently be accounted for by the presence of defects (vacancies) in the structure[77,83].

Table 1. X-ray diffraction data for rare-earth trifluorides[29,72–75].

Compound	Hexagonal unit cell parameters, Å		Density of hexagonal modification ($Z = 6$), g cm^{-3}	Temp. of polymorphic transformation, °C	Rhombohedral unit cell parameters, Å			Density of rhombohedral mofifications ($Z = 4$), g cm^{-3}
	a	c			a	b	c	
LaF_3	7.185	7.351	5.938	—	—	—	—	—
CeF_3	7.112	7.279	6.157	—	—	—	—	—
PrF_3	7.075	7.238	6.14	—	—	—	—	—
NdF_3	7.030	7.200	6.506	—	—	—	—	—
PmF_3	6.97	7.190	6.72	—	—	—	—	—
SmF_3	6.956	7.120	6.925	555	6.669	7.059	4.405	6.643
EuF_3	6.916	7.091	7.088	700	6.622	7.019	4.396	6.793
GdF_3	7.06*	7.20*	—	900	6.570	6.984	4.393	7.047
TbF_3	7.03*	7.10*	—	950	6.513	6.949	4.384	7.236
DyF_3	7.01*	7.05*	—	1030	6.460	6.906	4.376	4.465
HoF_3	6.833	6.984	7.829	1070	6.404	6.875	4.379	7.644
ErF_3	6.97*	8.27*	—	1075	6.354	6.848	4.380	7.814
TmF_3	6.763	6.927	8.220	1030	6.283	6.811	4.408	7.971
YbF_3	6.99*	8.32*	—	985	6.216	6.786	4.434	8.168
LuF_3	6.96*	8.30*	—	945	6.151	6.758	4.467	8.332
YF_3	7.13*	8.45*	—	1052	6.353	6.850	4.393	5.069

* The unit cell parameters are given at a temperature 10–15 deg above the polymorphic transition point[72].

The results of studies on the vibrational spectra of LaF_3, PrF_3, and NdF_3[84–86] agree with the X-ray diffraction data obtained by Zalkin et al.[75] and also by Mansmann[74]. The total number of bands in the Raman spectra of the single crystals of trifluorides belonging to the tysonite structural type, obtained on excitation with an argon laser, agrees with the theoretical analysis for a hexagonal unit cell with 6 formula units (space group $P\bar{3}c1$). Even at room temperature five bands associated with the fully symmetrical A_{1g} vibration and 12 bands corresponding to the degenerate vibrations (E_{1g} and E_{2g}) were observed in the Raman spectrum, in agreement with calculation for $P\bar{3}c1$ symmetry. In the reflection spectrum polarised parallel to the principal axis of the crystal

(region of A_{2u} type vibrations), four bands were found instead of the six postulated on the basis of the calculation, which may be attributed solely to a slight distortion of the LnF_3 structure compared with the more symmetrical model with the space group $P6_3/mcm$.[84]

Although the structural type persists in the LaF_3–CeF_3–PrF_3–NdF_3 series, a decrease of the ionic radii of the elements in this series leads to some distortion of their structure[79]. In consequence of the difference between the ionic radii of lanthanum and other lanthanides, the distortion of the crystal structure is demonstrated also by the ESR spectra of the impurity Ln^{3+} ions in LaF_3 single crystals[87–89]. Paramagnetic ions can substitute 6 non-equivalent lanthanum positions, but the local crystal field around them depends on the nature of the impurity ion, as can be seen from the change in angle formed by the z axis of the g-tensor and the c axis of the crystal[89].

The optical spectra of Ln^{3+} in LaF_3 show a large number of polarised lines, indicating a higher symmetry of the local crystal field operating on these ions in LaF_3[90,91] than would be expected for C_2 symmetry in the distribution of cations in the tysonite structure.

Orthorhombic rare-earth trifluorides crystallise with a structure of the YF_3 type (space group $Pnma$)[29], in which the metal is surrounded by 6 fluorine atoms located at the vertices of a trigonal prism and three fluorine atoms adjacent to the centres of its lateral faces. Eight fluorine atoms are at a distance of 2.3 Å from the metal (yttrium), while the ninth is at a distance of about 2.6 Å. The coordination polyhedron in YF_3 is linked to adjacent polyhedra by the triangular planes of the prism.

The chemical bonds in lanthanide trifluorides are significantly ionic. The amount of ionic character in such compounds, determined experimentally, agrees satisfactorily with the values calculated theoretically with the aid of overlap integrals and by the electronegativity method[92].

The predominantly ionic character of Ln–F bonds can be accounted for by the considerable size of the Ln^{3+} ions and the characteristics of their electronic structures; the formation of covalent bonds involving hybrid orbitals is difficult, because the $4f$ electrons are screened by the outer electron shells and their contribution to the formation of covalent bonds is slight. Nevertheless the presence of partial covalent character is probably due to their involvement (since there is no other possibility), which explains certain regularities in the crystal properties[93–95]. The ^{19}F NMR data on the delocalisation of $4f$ electrons in PrF_3 and NdF_3 also confirm the involvement of $4f$ electrons in the formation of chemical bonds[79]. Calculation of the spin–orbital parameters for Yb^{3+} (and Tm^{2+}) in CaF_2 also indicates the overlapping of the $4f$ and $5p$ levels with the fluorine orbitals[96].

3. Physicochemical Properties of Rare-earth Trifluorides

Table 2 lists certain thermodynamic functions of rare-earth fluorides taken from the literature[24,97–111]. Only the heat of formation of YF_3 ($\Delta H^\circ_{298} = -410 \pm 0.8$ kcal mole^{-1})[97] has been determined by direct combustion of the metal in a bomb calorimeter filled with fluorine[97]. The heats of formation of lanthanide trifluorides were obtained by indirect experimental methods using the heats of formation of the hydrated trifluorides[24,98] and also data obtained in a study of the equilibrium in the reaction between AlF_3 and fused rare-earth chlorides[99,100]. Numerous estimates of the ΔH for the trifluorides have been discussed[102].

The heat capacity of crystalline CeF_3 at 298°K is 22.34 cal mole^{-1} deg^{-1}. Its temperature variation has been described[112]. The entropy of crystalline CeF_3 is $\Delta S^\circ_{298} = 27.6$ e.u.[113] The estimated entropies of yttrium and lanthanum trifluorides are 21.5 and 23.3 e.u. respectively.

Rare-earth trifluorides are fairly refractory compounds (Table 2). With increase of the atomic number of the element, the melting points initially decrease and then, starting with ErF_3 (Toma and Brunton[72]) (with HoF_3, according to other data[57]), increase slightly. The minimum in the melting point curve for the trifluorides corresponds in all probability to the maximum in the polymorphic transition temperature curve [LnF_3(rhomb.) ⇌ LnF_3(hex.)][72].

Table 2. Heats of formation[24,97–101] and thermodynamic characteristics of the sublimation process[103–111].

Compound	M.p., °K (Ref.5)	$-\Delta H^\circ_{298}$ (form.)*, kcal mole^{-1}	ΔH° (subl.) (1470°K), kcal mole^{-1}	ΔS° (subl.) (1470°K), e.u.	ΔH°_{298} (subl.) kcal mole^{-1}	ΔS°_{298} (subl.), e.u.
LaF_3	1766	404, 405	99.5	44	107	40
			82	32	88	
CeF_3	1703	402	94	42	100	48
			92	40	92 (98)	
PrF_3	1668	401—402	97	43	107	54
			83	35	91	43
NdF_3	1667	398.9±0.5; 395	86	37	96	41
			82	33	87	
SmF_3	1579	390, 399	—	—	107	—
EuF_3	1549	375	—	—	101	—
GdF_3	1504	397.5±0.5; 389; 406.5±0.3	—	—	—	—
TbF_3	1445	(376—390)	—	—	—	—
DyF_3	1427	(371—407)	106 (1356° K)	49 (1356° K)	114	60
HoF_3	1416	(380—406)	106 (1366° K)	49 (1366° K)	113	59
ErF_3	1413	378, 389	107 (1373° K)	49 (1373° K)	114	60
TmF_3	1431	(366—378)	90 (1353° K)	38 (1353° K)	97	
YbF_3	1430	382	86 (1362° K)	36 (1362° K)	93	
LuF_3	1455	(365—372)	96 (1368° K)	43 (1368° K)	104	
YF_3	1425	410.7±0.8	100 (1332° K)	45 (1332° K)	115	

* The estimated values of ΔH are indicated in brackets (for further details, see Polyachënok[102]).

The heat of fusion of cerium trifluoride was determined as 13.2 kcal mole^{-1};[113] estimated data are available for other compounds[9]. The heats of fusion of DyF_3, HoF_3, and ErF_3 were found from the differences between the heats of evaporation and sublimation[109]. The densities of the fused trifluorides of lanthanum, cerium, praseodymium, samarium, and yttrium, have been published[114].

Close to the melting point, rare-earth fluorides exhibit an appreciable increase in volatility. The temperature variation of the sublimation pressures of the trifluorides has been described[103–111].

The sublimation pressures have been obtained by a torsion-effusion method (Suvorov[12,107] and Searcy and coworkers[103,108,111]) and by a mass-spectrophotometric method (Margrave and coworkers[104–106,109,110]). The absolute vapour pressures over the solid or fused trifluorides can be illustrated by the following examples (mmHg):

LaF_3 $2.2\cdot10^{-5}$—$3.7\cdot10^{-3}$ (1200—1405° K),
CeF_3 $3.7\cdot10^{-4}$—$1.5\cdot10^{-2}$ (1317—1500° K),
DyF_3 $1.1\cdot10^{-3}$—$8\cdot10^{-1}$ (1326—1622° K),
LuF_3 $9.65\cdot10^{-3}$ (1372° K)
YF_3 $1.5\cdot10^{-4}$—$2.1\cdot10^{-3}$ (1256—1434° K).

The heats of sublimation derived from these data are listed in Table 2.

The boiling points of the trifluorides vary from 2600°K (LaF_3) to 2500 °K (LuF_3).[9] The principal component of the gas phase over the solid and fused trifluorides is LnF_3

molecules[103,104,106-111]. Mass-spectrophotometric study of the composition of the gas phase established the presence of the ionic species Ln^+, LnF^+, and LnF_2^+, which are formed as a result of the dissociation of gaseous LnF_3 and not by simple ionisation of the gas-phase species with the corresponding composition. Neutral LnF and LnF_2 molecules have been detected in the LnF_3–Ln (and BaF_2–Nd) systems[104,105,115].

The results of electron-diffraction studies on gaseous lanthanum, neodymium, and yttrium trifluorides have been interpreted[116,117] on the hypothesis of a planar structure of the LnF_3 molecules with a triangular configuration. At the same time calculation of the valence state of these elements suggests a pyramidal structure of the trifluoride molecules with the rare-earth atom at the apex[118].

The estimated heats of formation (ΔH°_{298} kcal mole^{-1}) of gas-phase tri-, di-, and mono-fluorides of certain elements are listed below[104,115]:

	Nd	Sm	Eu	Gd	Dy	Ho	Er
LnF_3 (gas)	303	318	310	310	290	289	283
LnF_2 (gas)	159	160	160	162	157	157	150
LnF (gas)	36	164	58	40	36	40	35

The dissociation energies (D_{298}, kcal mole^{-1}) of the gaseous fluorides are, for example:

	Nd	Sm	Gd	Ho	Er
F_2Ln—F	165	160	150	151	152
FLn—F	143	138	143	136	134
Ln—F	130	127	141	123	136

Optical properties of rare-earth trifluorides. The hexagonal trifluorides exhibit very weak double refraction. The refractive indices increase in the series LaF_3–NdF_3 with the atomic number of the element. The orthorhombic trifluorides (from SmF_3 to LuF_3) have lower refractive indices than the hexagonal trifluorides. The refractive indices of the orthorhombic trifluorides hardly change in the above series[28,47,40]. Nevertheless the molar refractions of the trifluorides decrease linearly with the atomic number of the element, the curve describing the variation of R_M showing only a slight break on transition from the hexagonal to the orthorhombic group.

Lanthanum trifluoride is a valuable optical material, mainly for laser engineering. Single-crystal LaF_3 specimens exhibit high thermal and radiation stability and are transparent over a wide spectral range (from 120–130 nm to 13 nm)[119,120].

Lanthanum trifluoride constitutes a convenient base for the introduction of rare-earth activator ions, since the latter substitute lanthanum ions isomorphously. The isomorphous incorporation of triply charged ions into the LaF_3 structure does not require a charge compensation and therefore the spectroscopic properties of the Ln^{3+} present at a high concentration in such systems are determined largely by a single type of optical centre[68], as a result of which LaF_3 is a suitable material for the investigation of the optical spectra of the lanthanide ions[121-132]. The Ln^{3+} spectra in the visible region and the near ultraviolet, which are due to transitions within the well-screened 4*f* configuration, are comparatively little susceptible to the effect of the crystal field, which causes a splitting of the terms but has only an insignificant effect on the positions of their centres of gravity. A change in the type of chemical bond has a very significant effect on the positions of the centres of gravity of the energy levels of lanthanide ions, as can be seen, for example, from the La^{3+} spectra in the series lanthanum fluoride–lanthanum chloride–lanthanum bromide–lanthanum ethyl sulphate[133]. The same type of behaviour—a shift of the absorption bands towards the long-wavelength part of the spectrum with increasing degree of covalence of the bond—is observed in the transition $LnF_3 \rightarrow LnOF \rightarrow Ln_2O_3$.[134,135]

Keating and Drickamer[136] investigated the effect of a 50 000 atm pressure on the spectra of PrF_3 and NdF_3 crystals in the visible region and the near infrared. The authors explain the increase of the intensities of the individual bands in the spectra by an increase in the extent of interaction of 5*d* and 4*f* orbitals in the excited state as a result of the compression of the substance.

Certain rare-earth fluorides have been investigated to elucidate the possibility of their employment as optical coatings[137,138]. The chemical stability of the trifluorides in films, the pronounced abrasive quality of the coatings, and the possibility of their preparation in a crystalline form are valuable properties. However, the optical constants of the films (refractive indices, extinction coefficients) depend on the condensation conditions, particularly the temperature of the salt. Only films condensed on supports heated to about 300°C exhibit fairly constant properties and have a crystalline structure. The structure of the film varies with the thickness of the layer sputtered on to the support[139,140]. When lanthanum trifluoride is sputtered on to a heated support in a vacuum, an amorphous LaF_3 layer is formed initially and then a cryptocrystalline layer with an arbitrary orientation of the crystals. The succeeding layers have a preferred orientation, but its appearance does not affect the structure of the lower layers[140].

The electronic spectra of rare-earth trifluorides in films have been described[138,141].

The electrical properties of rare-earth trifluorides. The temperature variation of the conductivity of LaF_3 single crystals has been investigated in the range between 300° and 825°K.[83] Ionic conduction makes a large contribution owing to the mobility of fluoride ions. Because of this, LaF_3 single crystals may be used as indicator electrodes for the measurement of the activity of fluoride ions and for its potentiometric determination[142]. Electrodes with an active membrane of LaF_3 single crystals, which are selective in relation to F^- ions, have already found application and permit determinations down to 0.02 μg F ml^{-1} in various materials[143-145]. The introduction of the Eu^{2+} additive into LaF_3 results in a further increase of the electrical conductivity of the crystals[142].

The electrical properties of trifluoride films have been investigated in connection with the use of these materials for the preparation of film condensers[146].

The magnetic properties of rare-earth trifluorides have been described[51].

Chemical properties of rare-earth trifluorides. Under the usual conditions rare-earth trifluorides are stable in air and are non-hygroscopic, but their capacity to absorb moisture and gases from air increases appreciably with their degree of dispersion.

The trifluorides are rare-earth compounds which are least soluble in water and acids. Their solubility in water is approximately in the range 10^{-6}–10^{-5} M, the minimum values corresponding to the middle of the lanthanide series[147]. Yttrium trifluoride is more soluble than the trifluorides of the cerium group. As the pH is reduced (down to 2), the solubility of CeF_3 initially decreases somewhat and then rises sharply (down to pH 0).[148]

In HF solutions the solubility of the trifluorides also initially decreases with increasing acid concentration and then rises slightly[149,150]. The increase of the solubility of LaF_3 was observed starting with 55% HF solution[149]. The solubility of the trifluorides (CeF_3) in liquid hydrogen fluoride is low (≤ 0.04 g in 100 g of HF at 12°C).[151] In NH_4F solutions it is appreciably higher[152].

Rare-earth trifluorides can be dissolved by decomposing them with hot concentrated sulphuric acid, fusion with carbonates and alkalis, and also on heating with concentrated sodium hydroxide solution[153]. Moreover, they dissolve in solutions of Complexone III [disodium salt of EDTA (Ed. of Translation)][44] and certain metal salts, forming more stable complexes with F^- ions, for example, aluminium and beryllium[44,154,155]. An appreciable increase of the solubility of lanthanum and cerium trifluorides, associated with the formation of UO_2F^+ ions, was observed by Deichman and Tananaev[156] in solutions of uranyl nitrate. The solvent power of beryllium salts in relation to rare-earth fluorides is due to the formation of complexes, for example BeF^+,[154,157] which are only slightly dissociated. The formation of these complexes explains the incomplete isolation of rare-earth fluorides in the presence of beryllium in solution[158].

Lanthanum trifluoride reacts on standing with oxalic acid, forming insoluble stable lanthanum fluoride oxalate $La_2F_4C_2O_4$.[153]

Hydrofluoric acid or its salts precipitate trifluorides containing water from rare-earth salt solutions. The precipitates thus obtained are finely dispersed and contain between 0.3 and 1 mole of water per mole of LnF_3. The water content depends both on the nature of the element and the precipitation conditions, washing, and drying of the precipitates[22-24,37,159]. Readily filterable precipitates of more definite composition, $LnF_3.(0.4-0.5)H_2O$ (Ln = La, Pr, Nd, or Sm) are obtained by treating a suspension of rare-earth carbonates in water with an excess of hot hydrofluoric acid[37]. The compositions of the hydrated trifluorides of heavier elements (dysprosium, holmium, praseodymium, and ytterbium) are close to the formula $LnF_3.H_2O$.

It has been frequently noted[22,24,37] that water in trifluorides is energetically non-equivalent. Some of it is probably of the adsorption type and is removed at 40–100°C, while the remainder stays bound even above 300°C.

Refractometric and infrared absorption spectroscopic data for the trifluorides indicate the formation of OH–F hydrogen bonds[24,160]. The hydrated products contain the structures of the anhydrous trifluorides[161]. In the presence of 3–4% H_2O, the volume of the unit cell of the hexagonal trifluorides remains unchanged[37] but the density of water-containing specimens is much lower compared with the anhydrous compounds, indicating in all probability that they have a defect structure which is shown by the appearance of additional vacancies.

The ^1H NMR magnetic resonance spectrum (–130°C) of $LaF_3.nH_2O$ is consistent with the hypothesis of non-equivalent water molecules in trifluorides and indicates a diffusion-dependent mobility of the water in the structure. Its presence influences the mobility of F^- ions[23]. These results also confirm that the hydrated trifluorides have a defect structure.

The study of the solubility in $LnCl_3$–MF–H_2O systems (M = alkali metal and Ln = Er, Yb, or Lu) showed that, for the molar ratio $n = MF/LnF_3 = 1$, a precipitate is not deposited owing to the formation of soluble salts containing the LnF^{2+} complex ions. An increase of n to 3 leads to the formation of an LnF_3 precipitate (evidently hydrated).

When $n > 3$, the trifluorides are converted into double fluorides with the composition $MLn_2F_7.nH_2O$ or $M_2Ln_3F_{11}.nH_2O$.[162] A similar reaction mechanism obtains also in the precipitation of rare-earth ions by ammonium fluoride; the double fluorides $(NH_4)_2Ln_3F_{11}.nH_2O$ and $(NH_4)_4Ln_3F_{13}.nH_2O$ have been isolated from solutions containing an excess of ammonium fluoride[163]. Sodium fluorosilicate precipitates lanthanide ions in the form of their trifluorides[164,165].

Spectrophotometric study of rare-earth salt solutions containing alkali metal fluorides and carbonates showed the formation of the complex ions $Ln(CO_3)_3F^{4-}$, $Ln(CO_3)_2F_2^{3-}$, $LnCO_3F_3^{2-}$, and $LnCO_3F_2^-$.[166] Precipitates of the fluorocarbonates $LnCO_3F.nH_2O$ may be isolated from solutions with a high concentration of the ions and the molar ratios $Ln:CO_3:F = 1:1:1$.[166-168] With the ratios $Y:CO_3:F = 1:1:2$ and $1:1:3$, the compounds $KYCO_3F_2.1.5H_2O$ and $K_2YCO_3F_3.1.5H_2O$ respectively were obtained[168]. Analogous neodymium compounds have also been isolated[167].

In addition fluorocarbonates can be obtained by the reaction of calculated amounts of hydrofluoric acid with a suspension of rare-earth carbonates in water[167,170]. In nature these compounds form the mineral bastnaesite.

The solubility of rare-earth fluorocarbonates in water is about $(2-4) \times 10^{-5}$ M, increasing in potassium carbonate solutions[168]. The fluorocarbonates are dehydrated at 160–180°C; further heating leads to the decomposition of the compounds and terminates above 400°C with formation of oxide fluorides[169,171].

The stability of rare-earth fluoride complexes in solution. The triply charged lanthanide and yttrium ions form complex ions with fluorine which are less stable than the aluminium and scandium complexes (Table 3) but more stable than other halide complexes.

Table 3. Stability constants of the fluoride complexes MF^{2+}.

Element	$\lg\beta_1$			Element	$\lg\beta_1$		
	$I = 0$	$I = 0.5$	$I = 1$		$I = 0$	$I = 0.5$	$I = 1$
Al	—	6.32	—	Eu	—	—	3.19
Sc	—	6.18	—	Gd	4.26	3.37	3.31
Y	—	3.93	—	Tb	—	—	3.43
La	3.6	2.68	2.67	Dy	—	3.58	3.46
Ce	4.0	3.11	2.81	Ho	—	—	3.52
Pr	—	—	3.01	Er	—	3.53	3.54
Nd	—	—	3.09	Tm	—	—	3.56
Sm	—	—	3.12	Yb	—	3.60	3.58
				Lu	—	3.47	3.60

The stability constants of the LnF^{2+} complex ions, the main reaction product in the system $Ln^{3+} + HF \rightleftharpoons Ln^{2+} + H^+$, are listed below. They were taken from the literature[162-174]. (See in addition Refs. 175–180.)

The rare-earth fluoride complexes are of the inner-sphere type with a predominantly ionic type of bonding[174]. The relative stability of the LnF^{2+} complexes has been explained[174] by a large positive entropy of formation (Table 4).

As the Ln^{3+} ionic radius is reduced, the stability of the fluoride complexes (LnF^{2+}) increases, but the increase of K_{st} is non-monotonic. (See also the values of ΔF in Table 4.) Apart from the LnF^{2+} ions, the solution may contain the less stable complexes LnF_2^+ and LnF_3(aq.).

The reactions $Y^{3+} + HF \rightleftharpoons YF^{2+} + H^+$, $YF^{2+} + HF \rightleftharpoons YF_2^+ + H^+$, $YF_2^+ + HF \rightleftharpoons YF_3(aq.) + H^+$, and $YF_3 + HF \rightleftharpoons YF_4^- + H^+$ have been investigated for yttrium and their equilibrium constants have been determined (10.0, 2, 2, and 10 respectively) together with the stability constants of YF_2^+, $YF_3(aq.)$, and YF_4^-.[175]

Table 4. Thermodynamic quantities for the reactions $Ln^{3+} + F^- \rightleftharpoons LnF^{2+}$ (25°C, $I = 1$).

Element	$-\Delta F$, kcal mole^{-1}	ΔH, kcal mole^{-1}	ΔS, e.u.	Element	$-\Delta F$, kcal mole^{-1}	ΔH, kcal mole^{-1}	ΔS, e.u.
La	3.64	4.00	25.6	Tb	4.67	7.51	40.8
Ce	3.84	4.82	29.0	Dy	4.72	7.03	39.4
Pr	4.11	5.74	33.1	Ho	4.80	7.26	40.4
Nd	4.21	6.83	36.9	Er	4.83	7.43	41.2
Sm	4.25	9.39	45.8	Tm	4.86	8.66	45.4
Eu	4.35	9.22	45.4	Yb	4.89	9.56	48.5
Gd	4.52	8.90	45.1	Lu	4.93	9.53	48.5
				Y	4.91	8.32	44.5

The hydrolysis constants of the cerium fluoride complexes CeF^{2+} and CeF_2^+ have been estimated[181] as 3×10^{-7} and 4×10^{-10} respectively.

The existence of the complexes LaF^{2+}, LaF_2^+, and LaF_3 in the LiCl–KCl melt has also been established[182].

III. REACTIONS OF RARE-EARTH TRIFLUORIDES WITH THE FLUORIDES OF OTHER ELEMENTS

1. $MF-LnF_3$ Systems

The ratio of the ionic radii of M^+ and Ln^{3+} [183] or the ratio of the cationic field strengths[184] has been suggested as criterion of the formation of compounds in $MF-LnF_3$ systems. When $r_{M^+} : r_{Ln^{3+}} = 0.7$, the formation of compounds by the components is not to be expected at all; if the ratio is in the range 0.7–1.4, a compound $MLnF_4$ is formed and for a ratio of the cationic radii in excess of 1.40 the trifluorides form with alkali metal fluorides compounds having the composition M_3LnF_6.[183] Indeed in the $LiF-LaF_3$ (CeF_3, PrF_3) systems for which the ratio of the cationic radii is 0.64–0.67, no compounds of the components have been observed[185–188], while in systems with heavier elements in the samarium–lutetium series compounds with the composition $LiLnF_4$ are formed[134]. $NaF-LnF_3$ systems ($r_{M^+} : r_{Ln^{3+}} = 0.93–1.21$ give rise to the compounds $NaLnF_4$ [47,48,189] (which decompose in the solid phase possibly only in the case of the very last elements in the rare-earth–Na_3LnF_6 series[184]). In $KF-LnF_3$ systems there is a possibility of the formation not only of $KLnF_4$ but also of K_3LnF_6. There is no information about the formation of K_3LaF_6 in the corresponding system[190] but in all systems with other trifluorides compounds having this composition do exist. It is noteworthy that they are formed when the ratio of the cationic radii is appreciably less than 1.40, although in this case the compounds decompose in the solid phase.

With rubidium and caesium fluorides, all the rare-earth trifluorides apparently form compounds having the composition M_3LnF_6.[48,49,184,191] If the M_3LnF_6 compounds can be heated up to the melting point, they fuse without decomposition, the liquidus curves showing sharp maxima. It is striking that in systems where the M_3LnF_6 compounds are stable in the melt, the $MLnF_4$ compounds are stable only in the solid phase, whereas in the systems where the double fluorides $MLnF_4$ are in peritectic equilibrium with the melt, the M_3LnF_6 compounds decompose (if they are formed at all) without reaching the melting point[184].

The thermal stability of the M_3LnF_6 compounds increases in the series K–Rb–Cs.[48,184,191–194] In all the $CsF-LnF_3$ systems the congruently melting compounds Cs_3LnF_6 are formed, in the $RbF-LnF_3$ systems they are formed starting with PrF_3, and in the $KF-LnF_3$ systems their formation begins with SmF_3 (possibly with NdF_3).

The M_3LnF_6 fluorides may be obtained by fluorinating a mixture of MCl and $LnCl_3$ (or Ln_2O_3) in molar proportions of 3 : 1 at 400°C[195,196] or by sintering a mixture of the alkali metal fluoride and the rare-earth trifluoride in an evacuated tube and in an inert atmosphere (500–600°C)[197]. Compounds with mixed alkali metal cations A_2BLnF_6 and AB_2LnF_6 were synthesised by the same methods[198]. Moreover, K_3NdF_6 and even K_3LaF_6 were synthesised by dissolving the oxide of the corresponding element in the KBF_4–KCl melt[199].

The double fluoride of yttrium and potassium has a structure of the Rb_3TlF_6 type[195]; the tetragonal unit cell parameters are $a = 6.40$ Å and $c = 9.10$ Å ($z = 4$). The compound Cs_3YF_6 has the same structure as K_3YF_6.[195]

The double fluorides M_3CeF_6 and M_3PrF_6 and compounds with mixed alkali metal cations crystallise in the cubic system (of the distorted perovskite type)[195–198].

At 320°C K_3YF_6 undergoes a polymorphic transformation[192]. A polymorphic transformation has also been observed for K_3NdF_6 [200] and Rb_3PrF_6.[171] All the $MLnF_4$ compounds, except $LiTmF_5$, $LiYbF_4$, and $LiLuF_4$, are unstable in the melt or decompose on heating even in the solid phase.

The double fluorides of rare earths and lithium $LiLnF_4$ (Ln = Eu–Lu, Y) can also be obtained by the reaction of LiF and LnF_3 (or Ln_2O_3 in a stream of HF) at 400–450°C. These compounds have a structure of the scheelite type[201,202].

The nature of the interactions between the components in the $NaF-LnF_3$ systems and the products of this interaction have been investigated in greatest detail. The fusion diagrams for these systems have been studied up to 100 mole % LnF_3.[47] One of the compounds in the system is always $NaLnF_4$, which crystallises in the hexagonal system[203–206]. In the $NaF-LnF_3$ [207] and $NaF-CeF_3$ [208] systems the hexagonal modification of $NaLnF_4$ melts incongruently, forming a melt and LnF_3. In the $NaF-LnF_3$ systems (Ln = Pr–Gd) the incongruent fusion of $NaLnF_4$ results in the formation of a cubic phase, while in the systems containing the fluorides of elements ranging from terbium to lutetium the hexagonal modification initially becomes disordered and is then converted into a stoichiometric cubic phase[47].

A structural study of $NaNdF_4$ single crystals showed[209] that this compound is not of the β-Na_2ThF_6 structural type to which the $NaLaF_4$ and $NaCeF_4$ structures had been assigned previously[203,204]. The unit cell of $NaNdF_4$ contains 3/2 formula units and the cations are located in three different positions: the first contains neodymium ions (1 per cell), the second contains neodymium and sodium ions distributed at random (1/2 of each), and in the third sodium ions alternate at random with vacancies. The neodymium ions are surrounded by 9 fluoride ions, while in the β_2-Na_2ThF_6 structural type they should have a coordination number of 8.[209] The double fluorides $NaLnF_4$ of other rare earths have the same structures as $NaNdF_4$ (space group $P6$) or the structures are very similar[47,209,210].

Certain differences in the symmetry of the space group, which are observed on replacement of neodymium ions by those of other rare earths, can probably be accounted for by the partial mixing of the cations in various positions. The mineral gagarinite also has a structure similar to that of $NaNdF_4$.[211]

The cubic (high-temperature) modification of $NaLnF_4$ has a structure of the CaF_2 type; Na^+ and Ln^{3+} ions are distributed at random among the cationic sites in the crystal structure of this type[204]. Like CaF_2, the cubic phases exhibit wide regions of homogeneity, which include LnF_3.

Variable-composition phases are formed in the $NaF-LnF_3$ systems by the substitution of cations in the fluorite type structure (by Ln^{3+}) and the incorporation of additional fluoride ions in the vacancies of this structure[212]. This mechanism is confirmed by the calculation of the fraction of the molar free volume in the unit cell[47].

On formation of cubic solid solutions in the $NaF-LnF_3$ systems (Ln = Pr–Lu or Y), the upper limiting composition corresponds to the compound $Na_5Ln_9F_{32}$, which is the only congruently melting phase in systems containing the trifluorides of elements ranging from europium to lutetium[47,213]. The region of existence of disordered solid solutions expands as the ionic radius of the rare earth decreases. Their lower limiting composition varies from 55.5 mole % LnF_3 in the $NaF-PrF_3$ system to 39 mole % LnF_3 in the $NaF-LuF_3$ system[47]. The unit cell dimensions of the cubic $Na_5Ln_9F_{32}$ phases increase relative to those of the cubic stoichiometric double fluorides $NaLnF_4$.

The cubic solid solutions in the $NaF-LnF_3$ system are unstable below 500–800°C; the lowest temperature bounding the region of their coexistence corresponds to the system containing lutetium trifluoride. The cubic compound $Na_5Ln_9F_{32}$ in the $NaF-LnF_3$ systems (Ln = Pr–Tb) decomposes on cooling into the hexagonal form $NaLnF_4$ and the trifluoride of the corresponding element. In the $NaF-LnF_3$ systems (Ln = Dy–Lu), the $Na_5Ln_9F_{32}$ structure becomes ordered below 737–778°C with formation of an orthorhombic modification, which is also unstable on cooling below 700–450°C. The nature of the distortion of the unit cell is probably evidence of ordering in the distribution of the cations in the $Na_5Ln_9F_{32}$ structure. The cubic phases with the stoichiometric composition $NaLnF_4$ are converted into the hexagonal form below 600–700°C.[47,205,206]

The majority of the $KF-LnF_3$ systems have been only partly investigated[184,189,190]. The most complete data on the fusion and transformations in the solid phase are available for the $KF-YF_3$ system[194]. Apart from the compounds K_3YF_6 and KYF_4, the compounds KY_2F_7, KY_3F_{10}, and KY_7F_{22} were detected in the system[194,214]. The compound KY_2F_7 melts with decomposition at 890°C, forming a melt and KY_7F_{22}. The double fluoride KY_7F_{22} also melts incongruently with formation of a melt and yttrium trifluoride (965°C), while KY_3F_{10} decomposes in the solid phase at 795°C according to the equation $KY_3F_{10} \rightarrow KY_2F_7 + KY_7F_{22}$. Moreover, the formation of metastable solid solutions in the range between 62 and 90 mole % YF_3, the structure of which is derived from that of partly ordered fluorite, is characteristic of this system. When the solid solution is annealed (above 500°C), the structure is ordered further and the KY_2F_7, KY_3F_{10}, and KY_7F_{22} phases are segregated, the structures also being based on the CaF_2 type distorted in various ways.

Zachariasen[203,204] was the first to make an X-ray diffraction study of the compounds $KLnF_4$, using $KLaF_4$ and $KCeF_4$. He established that the double fluorides are dimorphic. The high-temperature modification has a structure similar to that of CaF_2, while the low-temperature modification was found[204] to crystallise in the hexagonal system like β_1-K_2UF_6. However, according to other data[217], the low-temperature modification of $KLaF_4$ has the same structure as $NaNdF_4$ and not β_1-K_2UF_6.

In the study of the $KF-CeF_3$ system, the hexagonal modification of $KCeF_4$ was not detected among the equilibrium phases[216]. Structural analysis of the single crystals of the low-temperature form of $KCeF_4$ obtained from the melt (35 mole % KF and 65 mole % CeF_3) established that they belong to the orthorhombic systems (space group *Pnma*, $a = 6.290$ Å, $b = 3.804$ Å, $c = 15.596$ Å, and $z = 4$).[216]

The double fluorides of the rare earths and alkali metals are incongruently soluble in water. In the $KF-CeF_3-H_2OF_6$ system (up to about 25% KF in the saturated solution) the solid phase contains cerium trifluoride[217]. With increase of the MF concentration, the stability in aqueous solution of the double fluorides of many rare earths increases[162,163,218].

An excess of sodium fluoride does not precipitate homogeneous products from solutions of the salts of the lightest lanthanides (La, Pr, Nd); hexagonal phases having almost the stoichiometric composition $NaLnF_4$ can be obtained in this way from solutions of samarium, europium, gadolinium, dysprosium, and holmium salts[219], while erbium, ytterbium, and lutetium ions are precipitated by an excess of sodium fluoride in the form of cubic fluorite-like phases with the composition $NaLn_2F_7.nH_2O$.[162] Potassium, rubidium, and caesium fluorides precipitate lanthanides (from Nd to Lu) in the form of phases which in the majority of cases are close in composition to the formula $M_2Ln_3F_{11}.nH_2O$.[162,163,219]

According to Ivanov-Emin et al.,[220] M_3LnF_6 and $MLnF_4$ can be obtained by the reaction of rare-earth bromides (or chlorides) with alkali metal fluorides in methanol solution.

The gas phase of the $NaF-YF_3$ and $NaF-LaF_3$ systems was found to contain, apart from NaF and LnF_3 molecules, also those of the compound $NaLnF_4$; there are data for the partial pressures of the components of the saturated vapour and the thermodynamic characteristics of the dissociation of $NaLnF_4$.[221,222]

2. MF_2-LnF_3 Systems

Most attention has been concentrated on systems containing rare-earth trifluorides and alkaline earth metal fluorides. The study of these systems is of practical importance in connection with the possibility of synthesising new phases having valuable optical, electrical, and magnetic properties. The isomorphism of alkaline earth metal fluorides and YF_3 (LaF_3, CeF_3), which has been known for a long time[223], is of especial crystal-chemical interest. An example of this type of isomorphism is provided by the minerals yttrocerite and yttrofluorite, which are widely distributed in nature.

Thermographic[224–231] and X-ray diffraction[232–237] data are now available for many MF_2-LnF_3 systems (M = Ca, Sr, or Ba). The formation by the components of solid solutions with the fluorite structure, the limits of the stability of which vary with the ratio of the cationic radii, is equally characteristic of all these systems. The phase diagrams for the MF_2-LnF_3 systems are usually classified in accordance with the capacity for the formation of other crystalline phases.

The phase diagrams for the MF_2–LnF_3 systems (Ln = La–Nd),[232,236] in which compounds are not formed by the components, are included in the first type. On the LnF_3 side, the systems are characterised by the formation of hexagonal solid solutions with the tysonite structure, which are stable approximately up to 15 mole % MF_2. In systems containing the trifluorides of elements ranging from samarium to dysprosium (holmium) (second type), the region of hexagonal solid solutions is limited on two sides by heterogeneous regions. The composition ~ $Ca_2Ln_5F_{19}$ (or $BaLn_3F_{11}$) corresponds to the limiting solid solution with the LaF_3 structure. As the ionic radius of the rare earth decreases, the region of existence of the hexagonal phase contracts. In the systems with BaF_2, such phases are more stable. On reducing the temperature, they decompose. The third type of diagram combines the systems containing the fluorides of the heaviest lanthanides (Er–Lu) and yttrium. The congruently melting compound $Ca_2Ln_5F_{19}$ (1156°C) is formed in the CaF_2–YF_3 system. Apart from the solid solutions of YF_3 and $Ca_2Ln_5F_{19}$ with the tysonite structure, the system was found to have a region of homogeneity between CaF_2 and $Ca_2Ln_5F_{19}$, the appearance of which is due to the ordering of the structure of the hexagonal phase[236]. A decrease of temperature leads to the contraction of the solid solution regions and their degeneration to a phase with a definite composition $Ca_2Ln_5F_{19}$ which decomposes at about 850°C into YF_3 and a cubic solid solution.

The congruently melting stoichiometric compounds $BaLn_2F_8$ and the incongruently melting phase with the probable composition $BaYF_5$ are formed in the BaF_2–YF_3 and BaF_2–LnF_3 systems, where Ln = Er–Lu. The crystals of the BaY_2F_8 and $BaTm_2F_8$ compounds belong to the monoclinic system (space group $C2/m$) and constitute a new structural type. Their structure consists of a framework of LnF_8 polyhedra connected edge to edge into six-membered rings forming channels in which are located barium atoms (coordination number 12)[238,239].

An exceptional feature of systems incorporating LnF_3 and alkaline earth metal fluorides is the high solubility of LnF_3 in MF_2 in the crystalline state, exceeding in some cases 50 mole % LnF_3. The solubility of LnF_3 in MF_2 increases with the ionic radius of Ln^{3+} also in the series CaF_2–SrF_2–BaF_2. The highest limiting concentration of LnF_3 is observed in the BaF_2–LaF_3 system and the lowest in the CaF_2–LuF_3 system[235]. With decrease of temperature, the stability of the cubic phases is higher the larger is the ionic radius ratio $M^{2+}:Ln^{3+}$.[234]

The unit cell parameters of the solid solutions with the fluorite structure in the CaF_2–LnF_3 systems increase and in the BaF_2–LnF_3 systems decrease with LnF_3 concentration: in the SrF_2–LnF_3 systems an increase in the unit cell dimensions occurs when the Ln^{3+} ionic radius is longer than that of neodymium. In the remaining cases the SrF_2 unit cell dimensions decrease. The substitution by strontium ions in the crystal lattice by neodymium ions does not lead to appreciable changes in the SrF_2 unit cell parameters[235]. In this case the increase of volume, associated with the filling of the free space in the cell by fluoride ions, is evidently compensated by the decrease due to the substitution of the larger cations by the smaller Nd^{3+} ions[234].

In order to explain the mechanism of the formation of solid solutions in the MF_2–LnF_3 systems, the measured crystal densities are frequently compared with the theoretical values for possible isomorphous substitution models. The agreement between the experimental values and those obtained on the hypothesis that additional fluoride ions are incorporated in the vacancies of the MF_2 structure as a result of the substitution of M^{2+} by Ln^{3+} constitutes fairly convincing proof of this type of mechanism[225,231,240]. To some extent it agrees with the ESR spectroscopic data for Ln^{3+} in MF_2 [241–246] and ^{19}F NMR data for CaF_2 containing cerium and ytterbium trifluorides[247]. X-Ray diffraction study of the $Ca_{0.6}Ce_{0.4}F_{2.4}$ single-crystal structure also made it possible to establish the presence in the solid solution of excess fluoride ions. However, their formation does not involve a simple incorporation of F^- ions in the centres of the cubic vacancies of the fluorite structure but the substitution of one ion in the initial structure by two (on substitution of one cation in the structure by Ln^{3+}), the additional ions being displaced along the space diagonal of the cubic vacancy to the extent of 1/6.[248]

The hexagonal solid solutions in the MF_2–LnF_3 systems have defect structures with anionic vacancies[231,234,237].

The study of the spectroscopic characteristics and induced emission parameters showed that activated crystals of solid solutions with the fluorite structure in the MF_2–LnF_3 systems have considerable advantages over simple fluorides and can be used to improve the efficiency of lasers[249–257]. The spectroscopic properties of solid solutions are associated with the characteristics of their structure, which is disordered. The random distribution of rare-earth ions among the cationic sites and the incorporation of fluoride ions in the vacancies of the crystal structure result in an abundance of centres, with various configurations of the surrounding species, where Ln^{3+} ions are located. Probably this is the cause of the broadening of the spectral lines. The removal of the structural degeneracy of the optical centres is also responsible for the weak concentration-dependent quenching of the Ln^{3+} luminescence. As regards their spectroscopic properties, these materials are intermediate between crystals and glasses. This can also be said of the ternary systems MF–MF_2–LnF_3.[203] The polythermal sections (CaF_2–$NaYF_4$ and CaF_2–$Na_2Ln_9F_{32}$) of the ternary systems revealed the formation of continuous solid solutions of the fluorite type. A decrease of temperature leads to an ordering of their structure[203]. Crystals of the CaF_2–$NaYF_4$ system have been used as the medium for lasers[258].

The fluorides of certain divalent elements, which crystallise with a structure of the fluorite type (CdF_2, EuF_2, PbF_2), also form variable-composition phases with rare-earth trifluorides. Fluorite-based solid solutions on the CdF_2 side and tysonite-based solid solutions on the LaF_3 side, separated by the heterogeneous region, have been found in the CdF_2–LaF_3 system, as in the case of CaF_2–LaF_3. With decrease of temperature, the solubility of LaF_3 in CaF_2 decreases appreciably and below 730°C the solid solutions decompose into the components. The hexagonal solid solutions are stable over a wide temperature range; the limiting solubility of CdF_2 in LaF_3 is 10 mole %. In the CdF_2–YbF_3 and CdF_2–YF_3 systems the limits of existence of the cubic solid solutions expand and at the same time there is an increase in the temperature range corresponding to the stability of the cubic phases—the decomposition of the solid solutions begins below 600°C.[259]

The formation of solid solutions in systems with cadmium fluoride involves the same mechanism as in the systems with alkaline earth metals[259,290]. Laser single crystals activated by neodymium have been obtained on the basis of cadmium fluoride containing up to 15 mole % YF_3.[261]

The study of the PbF_2–SmF_3 [262] and PbF_2–YF_3 [263] systems by thermal and X-ray diffraction analysis confirmed the formation of solid solutions.

In the PbF_2–CeF_3 system solid solutions with the CaF_2 structure exist up to about 60 mole % CeF_3. [240] The introduction of CeF_3 into PbF_2 does not affect its unit cell dimensions. Comparison of the experimental densities of the solid solutions in this system with the theoretical values for various types of isomorphous substitution is not inconsistent [240] with a model in which $3Pb^{2+}$ ions are substituted by two cerium ions with formation of cationic vacancies.

In the EuF_2–EuF_3 system [264] solid solutions based on the difluoride are stable up to 50 mole % EuF_3 (about 1300°C).

There is little information about the behaviour of rare-earth trifluorides in systems containing difluorides which do not crystallise with structures of the fluorite type. Data for the BeF_2–LaF_3 [190] and BeF_2–YF_3 [194,214] systems showed that beryllium fluoride in all probability does not form compounds with rare-earth trifluorides. Melts in systems incorporating beryllium fluoride show a tendency to form glasses. The glasses based on beryllium fluoride containing in addition alkali metal (and alkaline earth metal) fluorides are readily mixed with rare-earth trifluorides and the latter can be introduced at a high concentration. An advantage of these glasses is high transparency to ultraviolet light. The glasses formed in certain systems, for example in BeF_2–KF–YF_3–AlF_3, combine a high resistance to moisture with a low tendency towards crystallisation [194,265]. Beryllium fluoride glasses containing alkali metal fluorides, CaF_2, and AlF_3 are regarded as a possible material for lasers [265]. Their spectroscopic characteristics have been described and compared with those of oxygen glasses [266–271]. The principal characteristic of the spectra of Ln^{3+} in beryllium fluoride glasses is a narrowing of the luminescence band compared with oxygen glasses and a better resolution of the Stark components, probably associated with the weaker crystal field in the fluoride media. This results also in a smaller spectral width of the Nd^{3+} stimulated emission region compared with silicate glasses [266].

Certain features of the precipitation of rare-earth trifluorides from aqueous solutions in the presence of alkaline earth metal and other fluorides must be given special consideration. Khlopin and Merkulova [272] investigated the precipitation of RaF_2 with lanthanum trifluoride from aqueous solutions. They noted that, on reducing the concentration of the microcomponent in solution, the crystallisation coefficient tends to zero, i.e. there is a lower limit to miscibility. The presence of this limit was explained by the formation of solid solutions in which substitution in the crystal structure does not involve individual ions but whole blocks and consequently, in contrast to true homogeneous solid solutions, mixed crystals of this type may be regarded as quasi-homogeneous. It is noteworthy that radium fluoride is coprecipitated from the melt (KF–LaF_3 and RbF – LaF_3) [273] with lanthanum trifluoride, forming solid solutions without a lower limit to miscibility, which are evidently analogous to the tysonite phases in systems formed by rare-earth fluorides and alkaline earth metal fluorides. Possibly the mechanism of the coprecipitation of RaF_2 from aqueous solution with LaF_3 is based on the phenomenon of surface adsorption [274]. The appearance of a lower limit to miscibility can be accounted for from these standpoints using the concepts of statistical thermodynamics. According to this explanation, the condensed surface layer is fairly stable when the concentration of the microcomponent is above a certain critical value and can give rise to regions of its intrinsic crystal lattice during the growth of the crystal nuclei. Below this critical concentration of the microcomponent, the surface monolayer is unstable and should not be formed [275].

Data on the cocrystallisation of lanthanide and yttrium fluorides with alkaline earth metal fluorides from melts of the components have been presented [276–278] and the effect of the concentration of the microcomponent, the surrounding gaseous medium, and the ratio of the radii of the micro- and macro-components on the crystallisation coefficient have been discussed (see Klokman's review [279]).

The cocrystallisation of lanthanide and yttrium trifluorides with CaF_2 from solution obeys the homogeneous distribution law [280].

3. MF_3–LnF_3 and MF_4–LnF_3 Systems

Rare-earth trifluorides form solid solutions with one another and with the trifluorides of transuranic elements having the same structures. This property may be used to extract the tervalent rare earths formed in the fission of uranium, from fluoride melts with LnF_3 precipitates [281–283]. Small amounts of plutonium and neptunium are known to be capable of coprecipitating with lanthanum trifluoride, which gives rise to a method for the isolation of transuranic elements from solution on a carrier [284].

Rare-earth trifluorides in the hexagonal modification (of the tysonite type) form with one another a continuous series of solid solutions. The region of existence of the homogeneous tysonite phases with the orthorhombic trifluorides is limited and is narrower the greater is the difference between the ionic radii of the rare earths substituting one another in the unit cell. On formation of solid solutions of rare-earth trifluorides with one another and with the trifluorides of uranium and transuranic elements, the tervalent ions are distributed at random in the crystal structure. The unit cell parameters of the LaF_3(LnF_3) solid solutions decrease with increasing mole fraction of LnF_3. [285]

The interaction of rare-earth trifluorides with those of certain quadrivalent elements is of interest. The monograph of Seaborg and Katz [284] presents data on the almost quantitative coprecipitation of quadrivalent plutonium and neptunium from solutions with lanthanum trifluoride. In a study of the coprecipitation of quadrivalent thorium with LaF_3, Khlopin and Merkulova [286] concluded that they form anomalous solid solutions with a lower limit to miscibility. To confirm the possibility of the existence of solid solutions of rare-earth trifluorides and the tetrafluorides of cerium, thorium, zirconium, and uranium, Schlyter [285] undertook an X-ray diffraction study of the products of precipitation from solutions of their salts by sodium fluoride or hydrofluoric acid. He noted an appreciable decrease of the unit cell dimensions of lanthanum trifluoride precipitated in the presence of cerium and uranium salts; in the presence of thorium, the LaF_3 unit cell parameters remain unchanged, while in the presence of zirconium the decrease was very slight. The X-ray diffraction data for the precipitates thus suggest the formation of LaF_3–CeF_4(UF_4) solid solutions with a tysonite structure [285]. The decrease of the unit cell dimensions under these conditions might suggest that 4 lanthanum ions must be substituted by 3 M^{IV} ions with formation of cationic vacancies. However, thermographic and X-ray diffraction study of the CeF_3–CeF_4 system [287] did not confirm the presence of solid solutions of the components; the fusion diagram for this system is of the simple eutectic type and the interplanar

spacings and refractive indices of the compositions do not exhibit appreciable changes compared with CeF_3 and CeF_4. The coprecipitation of UF_4 (ThF_4) with rare-earth trifluorides from fluoride melts also has not been observed[281]. Possibly the coprecipitation of quadrivalent elements with LaF_3 is a property of aqueous systems only, since under these conditions finely dispersed precipitates with a high adsorption capacity are produced. The question of the behaviour of rare-earth trifluorides in systems containing the fluorides of quadrivalent elements apparently requires elucidation.

IV. RARE-EARTH OXIDE FLUORIDES

When the trifluorides are heated to 450–800°C, they react with atmospheric moisture with elimination of HF as a result of pyrohydrolysis. The intermediates in this reaction are oxide fluorides which on further interaction with water vapour are converted into the oxides (Ln_2O_3).[44,288] The pyrohydrolysis of the trifluorides at the beginning of the lanthanide series takes place at a higher temperature than for the heavier lanthanides and YF_3. Thus, by heating lanthanum and neodymium trifluorides in the presence of water vapour at 800°C, the stoichiometric oxide fluorides LnOF are obtained[289-292], whereas under the same conditions the trifluorides of dysprosium, holmium, erbium, and ytterbium can be fully converted into the oxides; it is sufficient to heat the trifluorides of these elements to 450°C in order to obtain their oxide fluorides.

Rare-earth oxide fluorides can also be obtained by the reaction of the trifluorides and oxides of the elements (at about 1000°C) in a vacuum or in an inert atmosphere[293-297]. The formation of lanthanum oxide fluoride was observed on dissolution of lanthanum hydroxide in lithium or sodium fluoride melts[298] and in the reaction between Ln_2O_3 and NHF_4.[299] They can also be obtained by the decomposition of the rare-earth fluorocarbonates (400–500°C)[169,171].

Zachariasen established[289] by X-ray diffraction of the pyrohydrolysis products of LaF_3 (900°C) and YF_3 (450°C) that in the initial stage a tetragonal phase is formed with a wide region of homogeneity, whose composition can be expressed by the formula $LnO_nF_{3n-2}(1 > n > 0.7)$. When $n = 1$, the tetragonal phase is unstable and is converted into a rhombohedral phase. The rhombohedral oxide fluorides of all rare earths[290-293,297], except CeOF, can be obtained by the pyrohydrolytic method. The pyrohydrolysis of CeF_3 in moist ammonia[290,300] and also the reaction of cerium dioxide with CeF_3 [301,302] (or a mixture of cerium, CeF_3, and CeO_2)[303] always gives rise to a cubic fluorite-like phase. As a result of the departure of its composition from stoichiometry, the unit cell parameter varies from 5.66 to 5.73 Å.[301-303] The structure of the variable-composition cubic phase contains both tervalent and quadrivalent cerium ions. At 1150°C the limiting solubility of CeO_2 in CeF_3 corresponds to the composition $CeO_{1.1}F_{0.9}$ ($a = 5.68$ Å).[303] The rhombohedral modification of CeOF can be obtained by the reaction of Ce_2O_3 and CeF_3 in a vacuum (1150°C)[302].

The rhombohedral LnOF phases (space group $R\bar{3}m$, $z = 2$) have the stoichiometric composition (or a very narrow region of homogeneity). The unit cell dimensions of the oxide fluorides are listed in Table 5.

On heating above 500–600°C the rhombohedral oxide fluorides undergo the reversible transformation of $LnOF_{rhombohedr} \rightleftharpoons LnOF_{cubic}$. In general the polymorphic transformation temperature changes only slightly in the lanthanide series (494°C for LaOF, 524°C for NdOF, 588°C for HoOF, and 592°C for ErOF).[296] At high temperatures the oxide fluorides decompose with evolution of gaseous LnF_3.[296] At room temperature the cubic oxide fluorides are metastable but can be obtained from elements ranging from lanthanum to europium by cooling the products of the reaction of LnF_3 and Ln_2O_3 at 800–1200°C.[293-296]

The cubic oxide fluoride phases have a structure of the CaF_2 type and are characterised by a random distribution of oxygen and fluoride ions among the anionic sites of the crystal lattice of this type. At room temperature it is stabilised by crystal lattice defects[296,304,305], i.e. the F^- ions incorporated in the vacancies. It is striking that the formation of the cubic phase has been detected in a study of the pyrohydrolysis products of NdF_3 (and PrF_3) for compositions very close to stoichiometry but with an excess of the fluoride[306]. The rigorously stoichiometric oxide fluorides are rapidly converted into the low-temperature form on cooling and it is apparently difficult to obtain their cubic phases by quenching[307].

Table 5. X-ray diffraction data for rhombohedral rare-earth oxide fluorides[289-291,295,297].

Compound	a, Å	$\alpha°$	d(X-ray), g cm^{-3}	Compound	a, Å	$\alpha°$	d(X-ray), g cm^{-3}
LaOF	7.132	33.01	6.02	TbOF	6.751	33.09	7.89
PrOF	7.016	33.03	6.39	DyOF	6.685	33.10	8.25
NdOF	6.953	33.04	6.69	HoOF	6.637	33.16	8.52
SmOF	6.865	33.07	7.19	ErOF	6.625	33.21	8.65
EuOF	6.827	33.05	7.37	YbOF	6.545	33.30	9.18
GdOF	6.800	33.05	7.67	YOF	6.697	33.20	5.14

An increase in the number of interstitial defects, i.e. an increase of the concentration of LnF_3 in LnOF, leads to a more ordered distribution of anions, characteristic of the tetragonal phase in the structure of which the oxygen and fluoride ions form alternating layers[289].

In general the region of existence of the tetragonal phase becomes narrower on increasing the atomic number of the cation[296]. The unit cell dimensions of the LnO_nF_{3n-2} tetragonal phase increase as n diminishes[288,296]. However, it should be borne in mind that the data of recent investigations of the phase diagrams of the oxide fluorides[307-309] by high-temperature X-ray diffraction analysis, by annealing the phases obtained at a high temperature, and by synthesising the oxide fluoride single crystals show that the diagrams are still more complex. In particular, the existence, at least in certain systems, of wide tetragonal phase regions is doubtful. In systems containing the oxide fluorides of elements ranging from samarium (and also yttrium) the tetragonal phases have a narrow region of homogeneity or are altogether absent. Moreover, even in systems containing the oxide fluorides of the elements at the beginning of the lanthanide series the region of tetragonal solid solutions is separated from those of the cubic and rhombohedral phases by a two-phase region. At about 700°C it is converted into a phase belonging to a crystal system of lower symmetry. In addition, in some systems the rhombohedral phases LnO_nF_{3n-2} with $n \simeq 0.6$–0.8 have been found in certain systems at a high temperature[307]. Possibly many systems do not contain homo-

geneous regions but discrete ordered (orthorhombic) phases, whose composition may be expressed by the general formula $(Ln_xO_{x-1}F_{x+2})_4$. The single crystals of the oxide fluorides of certain elements having this composition having been synthesised, for example $Y_{28}O_{24}F_{36}$ and $Er_{20}O_{16}F_{18}$. The structures of these phases are characterised by a unit cell comprising several layers of fluorite cells (7 in yttrium oxide fluoride and 5 in erbium oxide fluoride)[308].

In the crystal structures of the oxide fluorides the rare-earth ions can substitute one another. Such mixed phases have been investigated for the CeF_3–La_2O_3 (Pr_2O_3, Y_2O_3) systems. The following regions of homogeneity have been found in these systems: 14–60 mole % La_2O_3, 20–55 mole % Pr_2O_3, and 34–55 mole % Y_2O_3.[310] The cubic unit cell parameters (CaF_2 structural type) for equimolar compositions are 5.765 Å ($CeLa_2O_3F_3$) and 5.675 Å ($CePr_2O_3F_3$). $CeY_2O_3F_3$ has a rhombohedral unit cell ($a = 6.72$ Å; $\alpha = 30°20'$, $z = 2$). In the solid solutions of these systems either the vacancies are filled (when the fluorine content is less than in the equimolecular product) or anionic vacancies are formed (when the fluorine content is greater than in the equimolecular product).

Cerium trifluoride (and probably the trifluorides of other rare earths) forms non-stoichiometric phases also with oxides of bi- and quadri-valent metals. ThO_2 dissolves up to 62.5 mole % CeF_3. The formation of solid solutions with a cubic fluorite-type structure in this system is accompanied by the filling of the vacancies by fluoride ions. With increase of the content of dissolved CeF_3, the ThO_2 unit cell parameter increases from 5.0 to 5.78 Å.

Cerium trifluoride forms with the oxides of bivalent elements (MgO, CaO, SrO, BaO) solid solutions in the ranges 25–65% MgO, 35–80% CaO, 30–67% BaO, and 25–70% SrO. In the CeF_3–MgO (CaO) and CeF_3–SrO systems the crystals of the solid solutions belong to the orthorhombic system ($z = 2$). Depending on the compositions of the solid solutions of CeF_3 and MgO, the crystal structure contains an excess or a deficiency of cations, while in the crystal structure of the CeF_3(SrO) solid solutions there is an excess or a deficiency of anions. This mechanism is also characteristic of the formation of cubic fluorite-type solid solutions of CeF_3 and BaO [the unit cell parameter of the phase with equimolecular composition ($CeBaOF_3$) is 6.12 Å].[310]

The oxide fluorides of the rare earths and lithium $LiLnOF_2$ have been obtained by the pyrohydrolysis of mixtures of LiF and LnF_3 (or by heating compressed LiF and LnOF discs)[297].

Rare-earth chalcogenide fluorides. By sintering rare-earth sesquisulphides and trifluorides at 450–1000°C in evacuated sealed tubes, the sulphide fluorides LnSF may be obtained[311–314]. The sulphide fluorides of elements ranging from lanthanum to erbium crystallise with a structure of the PbClF type. The compounds YSF, HoSF, and ErSF are dimorphic. The crystals of their second modification (and also of YbSF and LuSF) belong to the hexagonal system (the structural type is unknown). Lanthanum selenide fluoride LaSeF crystallises in the orthorhombic system[312].

Variable-composition sulphide fluorides and selenide fluorides have been found in the CeF_3–MS and CeF_3–MSe systems (M = Ca, Sr, or Ba). The structures of the solid solutions produced in these systems are derived from that of fluorite distorted to different extents. The nature of the substitution of ions in their formation is similar to that in the CeF_3–MF_2(MO) systems[315].

V. FLUORIDES OF BIVALENT AND QUADRIVALENT RARE EARTHS

Compounds with the rare earths in the bivalent state are known for samarium, europium, thulium, and ytterbium. Of the difluorides, SmF_2, EuF_2, and YbF_2 have now been obtained in a pure form. They are synthesised by reducing the trifluorides with hydrogen[316–319] or by the corresponding rare-earth metal[320,321] at a high temperature. Reduction with hydrogen (1300–1400°C) yields only europium difluoride with a composition close to the stoichiometric formula. Stoichiometric samarium and ytterbium difluorides could not be obtained by this procedure. The composition of samarium fluoride obtained by the reduction of SmF_3 varies from $SmF_{2.3}$ to $SmF_{2.5}$. Similarly an F : Yb ratio less than 2.24 was not obtained in the product of the reduction of ytterbium trifluoride with hydrogen[319]. The stoichiometric difluorides of these elements can be obtained by the reduction of the trifluorides by the metal thermite method (1500–1900°C) in sealed molybdenum or tantalum crucibles. Thulium can be reduced in the same way, although pure thulium difluoride has not been obtained[321]. The bivalent metal fluorides can also be prepared by the double decomposition of a solution of Ln^{II} sulphate and sodium or ammonium fluoride in an atmosphere of an inert gas[319,322].

Rare-earth difluorides crystallise with a fluorite-type structure[323] and like fluorite form with rare-earth (and also aluminium) trifluorides solid solutions involving the filling of the vacancies[264,320,324]. This in fact accounts for the non-stoichiometric composition of the difluorides and the variability of their unit cell parameters quoted in different studies. For the same reason, the experimental values of the effective magnetic moment of EuF_2 differ from the theoretical value[318]. The antiferromagnetic ordering observed in EuF_2 is also associated with its contamination[325–327].

Cubic solid solutions based on the fluorite structure exist in the range $LnF_{2.0}$–$LnF_{2.25}$.[321] The unit cell parameters vary under these conditions from 5.87 to 5.84 Å (Sm), from 5.84 to 5.81 Å (Eu), and from 5.60 to 5.57 Å (Yb). A phase having a different structure was detected in the LnF_2–LnF_3 systems for the ratios F : Ln = 2.25–2.45.[321] Mössbauer spectra indicate the presence of Eu^{2+} and Eu^{3+} ions in the structure of the cubic phases and density measurements confirm the mechanism of their formation involving the insertion of the anions[321].

Rare-earth difluorides melt at a higher temperature than the trifluorides (above 1400°C)[325]. The compounds $MLnF_3$ are apparently formed with alkali metal fluorides. The double fluoride $CsEuF_3$ has the perovskite structure[328]. Europium difluoride forms with AlF_3 the compound $EuAlF_5$ which has the same structure as $SrAlF_5$.[324]

The bivalent state in the fluoride compounds of other rare earths can be achieved by irradiating with X-rays alkaline earth metal fluoride crystals activated with Ln^{3+}.[329,330] The reduction to doubly charged lanthanide ions is also possible by chemical methods[331], electrolysis in the solid phase[332–334], or by the action of powerful light pulses[335]. Lanthanum, neodymium, dysprosium, holmium, erbium, and thulium have been obtained in the bivalent state in fluoride matrices and investigated by physical methods. Under the action of radiation and on heating $CaF_2(Ln^{3+})$ crystals in an electric field, only some of the Ln^{3+} ions pass to the bivalent state. The percentage reduction of Ln^{3+} to Ln^{2+} depends on the radiation dose and the concentration of activator ions[336]. On average, the conversion reaches 5–10%. An appreciable increase in

the efficiency of the reduction has been achieved by heating $CaF_2(Ln^{3+})$ crystals in alkaline earth metal vapour at 750–950°C (the "additive") method. In this case it is possible to convert into the bivalent state up to 50–70% of neodymium, dysprosium, holmium, erbium, and thulium ions[337], which exhibit high stability to the action of light and heat[331,333,338,339].

The study of the optical spectra of Ln^{2+} in alkaline earth metal fluorides (and in other matrices) is of practical importance in connection with the problem of lasers. This field has been particularly developed in the work of Feofilov and coworkers[330,340]. Stimulated emission both under pulsed and continuous conditions has been achieved with bivalent rare-earth ions. The $CaF_2(Dy^{2+})$ laser, which has the smallest threshhold power, is of a special interest.

The local crystal field around Ln^{2+} in MF_2 has a high symmetry. The replacement of fluorine by other halogens (Cl, Br, I) should result in a lowering of the symmetry of the environment and the removal of the degeneracy of the levels[340]. A narrow luminescence band has been obtained for mixed MFHal crystals of this type activated with Dy^{2+}.[341]

The adsorption and luminescence spectra of Sm^{2+} and Tm^{2+} in beryllium fluoride glasses have been investigated[342,343]. The doubly charged ions in glasses based on beryllium fluoride are stable and are not oxidised on heating up to temperatures corresponding to the softening of the glasses.

The quadrivalent state is characteristic of cerium, praseodymium, and terbium, which can be obtained in the form of tetrafluorides or their double compounds with alkali metal fluorides. Quadrivalent neodymium and dysprosium have also been obtained in the form of complexes.

Anhydrous cerium tetrafluoride can be prepared by fluorinating cerium dioxide or cerium trifluoride[344,345]. The purest fluoride is obtained when elemental fluorine is employed as the fluorinating agent (350–500°C [346]). Hydrofluorination (with HF) of cerium dioxide at 250–325°C leads to a product containing a small amount of oxygen (possibly water) and at 400°C to phases whose composition varies from $CeF_{3.14}$ to $CeF_{3.87}$.[346] Anhydrous cerium trifluoride interacts with bromine trifluoride, but a stoichiometric product is not obtained, its maximum fluorine content corresponding to the formula $CeF_{3.83}$. Cerium tetrafluoride crystallises with a structure of the UF_4 type (monoclinic unit cell with the parameters $a = 12.60$ Å, $b = 10.60$ Å, $c = 8.30$ Å, and $\beta = 126°$).[347] The ^{19}F NMR spectrum of powdered CeF_4 showed line splitting above 287°K, which was tentatively explained by a structural transformation of the tetrafluoride[348].

In a neutral atmosphere cerium tetrafluoride is stable at the normal pressure up to 550°C. Above this temperature the tetrafluoride decomposes appreciably with evolution of fluorine and also sublimes. In a vacuum cerium tetrafluoride decomposes above 230°C.[349] Hydrogen reduces CeF_4 at 200–300°C. Cerium tetrafluoride reacts with the dioxide at 400°C, forming the trifluoride: $3CeF_4 + CeO_2 \rightarrow 4CeF_3 + O_2$. In dry oxygen cerium tetrafluoride is stable up to 700°C. Moist oxygen decomposes it at 500°C with formation of cerium trifluoride and dioxide. At 1000°C water vapour hydrolyses CeF_4 quantitatively to CeO_2. Cerium tetrafluoride is insoluble in water, but the latter gradually decomposes it to CeF_3. By dissolving cerium dioxide in an excess of hydrofluoric acid, it is possible to obtain the hydrate $CeF_4.H_2O$. Its structure differs from that of the anhydrous tetrafluoride[346]. When it is dehydrated at 200°C in a vacuum, the $CeF_4.0.3H_2O$ phase is formed without appreciable structural changes. In an inert atmosphere the hydroxide continuously loses weight between 80° and 440°C and is converted into CeF_3. It cannot be completely dehydrated without loss of fluorine[346].

The solubility of CeF_4 in liquid hydrogen fluoride (0.1 g in 100 g of HF) is higher than that of CeF_3.[151] The results of various workers[350,351] for the composition of the solid phase in equilibrium with the saturated solution at high HF concentrations and data concerning the possible existence of $CeF_4.HF$ are contradictory.

Fluorination of a mixture of alkali metal chlorides and cerium dioxide in molar proportions of 2 : 1 and 3 : 1 at 400–500°C yields compounds with the compositions M_2CeF_6 and M_3CeF_7.[352,353] The analogous compounds with ammonium fluoride can be obtained by allowing a concentrated NH_4F solution to react with hydrated cerium tetrafluoride; for the ratio $z = NH_4F : CeF_4 \geq 5$, the product is $(NH_4)_3CeF_7$, whereas with z between 2 and 5, $(NH_4)_2CeF_6$ is formed. If the ratio $z \leq 2$, the precipitate formed in the reaction has the composition NH_4CeF_5.[354] According to Penneman and Rosenzweig[355], in the CeF_4–NH_4F–H_2O system at 25°C the solid phase with the highest ammonium fluoride content is $(NH_4)_4CeF_8$, which is stable in the concentration range 28.9–45 wt.% NH_4F in the saturated solution. This compound was to be expected on the basis of refractometric measurements and by analogy with the UF_4–NH_4F system.[356] In addition, the fluoride $(NH_4)_7Ce_6F_{31}$ was obtained from solutions at a low NH_4F concentration (1%)[355] and the reaction of CeO_2 and NH_4F at 200°C gave $NH_4Ce_2F_9$.[346]

The reaction of CeF_4 with alkaline earth metal and lead fluorides gives the compounds $MCeF_6$.[357,358] One of the methods for their preparation involves the reaction of hydrofluoric acid with CeO_2 in the presence of the corresponding metal carbonate or the fluorination of a mixture of CeF_4 and the alkaline earth metal chloride (at 100°C). With the exception of Na_3CeF_7 and $(NH_4)_3CeF_7$, the compounds M_3CeF_7 crystallise in the cubic system and the compounds M_2CeF_6 in the hexagonal system of the type characteristic of modifications of uranium fluoride complexes[352,353]. The majority of the fluorides were investigated by X-ray diffraction in powder form. Revision of the crystal structure, for example of that of $(NH_4)_2CeF_6$, after preparing the single crystals established that this compound belongs to a system of lower symmetry[359] (space group $Pbcn$; $a = 7.03$ Å, $b = 12.10$ Å, and $c = 7.44$ Å). The double fluorides of cerium(IV) and alkaline earth metals and lead crystallise with a structure of the tysonite type. In the crystal structures of these compounds the cerium and M^{2+} ions are distributed at random among the cationic sites[358].

Double compounds of cerium are incongruently soluble in water[360,361]. The cerium ammonium double fluoride $(NH_4)_4CeF_8$ is immediately converted on heating into $(NH_4)_2CeF_6$, which decomposes at 240°C with formation of NH_4CeF_5. The final thermal decomposition product is cerium trifluoride.

In contrast to CeF_4, praseodymium tetrafluoride cannot be obtained in a pure form by high-temperature fluorination with elemental fluorine[349], although it is stable in the form of compounds with alkali metal fluorides[316,362,365] or in the form of solid solutions with CeF_4 obtained by fluorinating a mixture of CeF_3 and PrF_3.[316] The only method for the preparation of pure PrF_4 is the decomposition of Na_2PrF_6 with liquid hydrogen fluoride[366]. The method involves the extraction of sodium fluoride and it is recommended that the extraction be performed in the presence of gaseous fluorine[367] to avoid the contamination of PrF_4 with praseo-

dymium trifluoride. The effective magnetic moment of the tetrafluoride thus obtained agrees with the theoretical value[368].

Praseodymium tetrafluoride has the same structure as CeF_4 ($a = 12.47$ Å, $b = 10.54$ Å, $c = 8.18$ Å, and $\beta = 126.4$). [367] Compounds of the tetrafluoride with alkali metal fluorides can be obtained by fluorinating mixtures of MCl and Pr_6O_{11} (400–500°C)[362] or of PrF_3 and MF (450°C)[367]. Depending on the proportions of the components in the initial mixture, the compounds M_3PrF_7, M_2PrF_6, $MPrF_5$, and $M_7Pr_6F_{31}$ are formed. The quadrivalent state of praseodymium in these compounds has been confirmed by chemical[362,363], spectrophotometric[362,363,369,370], and magnetic methods[363].

Fluoropraseodymates have the same structures as the analogous uranium tetrafluoride compounds; Na_2PrF_6 crystallises in the orthorhombic system (space group *Immm*) like γ-Na_2UF_6, while $Na_7Pr_6F_{31}$ has the same structure as the rhombohedral fluoride $Na_7U_6F_{31}$. [367]

Terbium(IV) fluoride has been obtained by the reaction of its trifluoride with elemental fluorine (300–500°C). [349] It crystallises with a UF_4 type structure, like CeF_4 and PrF_4. A compound of TbF_4 with caesium fluoride (Cs_3TbF_7)[352,363,371], crystallising in the cubic system, has been obtained. Fluoroterbates analogous to Cs_2CeF_6 and Cs_2PrF_6 could not be obtained[371].

All the compounds of quadrivalent praseodymium and terbium are stable only in dry air and at room temperature. The majority of fluoropraseodymates are decomposed by water with formation of hydrated praseodymium(III) fluorides or double fluorides[363,364]. Their thermal stability may be increased to 1200°C by the formation of solid solutions with fluorozirconates, fluoroniobates, etc.[365]

The quadrivalent state can probably be achieved for neodymium and dysprosium in the form of compounds with caesium fluoride[316,352,364]. The compositions of these compounds are approximately represented by the formulae Cs_3NdF_7 and Cs_3DyF_7. [364,372] According to magnetic measurements, about half the dysprosium atoms in the compound $Cs_3DyF_{6.7}$ are in the quadrivalent state.

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Progress in the Halogenation of Organic Silicon Compounds

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The Review deals mainly with the direct halogenation of organic silicon compounds by halogens and halogenated compounds as among the most important methods for the preparation of organosilicon compounds containing halogen in the organic radicals. With respect to preparative possibilities, experimental simplicity, and in individual cases the yields obtained, the direct chlorination and bromination of organic silicon compounds has no equal. The preparation of halogenated alkyl (and aryl) silanes by various methods has been partly covered in previous monographs and reviews[1-8], but the direct halogenation of organic halogenosilanes has not yet been adequately reported in the review literature. The present paper makes an attempt to fill this gap. It gives a detailed discussion of the conditions and the mechanisms of radical halogenation (mainly with chlorination as example) under the influence of various initiators (ultraviolet radiation, peroxides, azo-compounds, γ-rays), and also electrophilic substitution and cleavage of the silicon-carbon bond in aryl- and alkylaryl-chlorosilanes. Besides substitutive halogenation, involving replacement of hydrogen in organic radicals by halogen atoms, the addition of halogen at double bonds present in these radicals is also surveyed. A list of 335 references is included.

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I. INTRODUCTION

Typical polysiloxane materials, despite their valuable technical properties, are no longer able at present to satisfy completely the increasing demands of modern technology, especially with respect to stability to heat and thermal oxidation, resistance to oils and fuels, lubricating and adhesive properties, etc.

A promising method for the controlled modification of the properties of polyorganosiloxanes is to introduce functional groups into the organic radicals framing the siloxane chains. The presence of a polar substituent in a hydrocarbon radical attached to a silicon atom increases the polarity of the polymer molecule and therefore improves the adhesion, mechanical strength, and other properties of practical importance.

The production of modified organosilicon polymers of this type demands appropriate monomers with functional groups, primarily halogeno-derivatives (especially chloro-derivatives) of various alkyl- and aryl-chlorosilanes. These are convenient initial compounds for obtaining other carbon functions of silicon—amines, nitriles, alcohols, acids, thiols, thiocyanates, etc. This is probably the reason for the rapid development of research on the halogenation of various organosilicon compounds.

Before examining the halogenation of organic silicon compounds we must consider certain specific properties of silicon, distinguishing it from carbon and resulting from the intermediate position which it occupies between this typical non-metal and the Group IV metals (germanium, tin, lead). This is important for a correct understanding of the influence of these characteristics on the reactivity of silicon–carbon and silicon–halogen bonds (compared with carbon–carbon and carbon–halogen bonds), which must be taken into account in order to accomplish the halogenation of organosilicon compounds.

II. SOME SPECIFIC FEATURES OF THE SILICON ATOM INFLUENCING THE REACTIVITY OF ITS ORGANIC COMPOUNDS

While occupying a position between carbon and germanium in the Periodic System, silicon is closer to the latter in most of its properties[4,6] (see Table).

Physical properties of the elements—carbon, silicon, and germanium—and their bonds with carbon and chlorine.

Element	Nuclear charge	Electronic structure	Covalent radius	Electronegativity (Ref.9)	Coordination No.	Energy of bond, kcal mole^{-1}, with		Ionic character of bond with Cl, %
						carbon	chlorine	
Carbon	6	$1s^2 2s^2 2p^2$	0.77	2.5	4	84.9	77.9	6
Silicon	14	$1s^2 2s^2 2p^6 3s^2 3p^2$	1.17	1.8	6	75.0	90.3	30
Germanium	32	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^2$	1.22	1.7	6			

By readily donating its valency electrons, the silicon atom is more liable to be attacked by various reagents than is the carbon atom in compounds of similar structure.

The comparatively high energy of the silicon–chlorine bond in chlorosilanes is explained by the considerably lower electronegativity of the silicon atom compared with carbon, which, combined with the great polarisability of the electron sheath of the silicon atom, ensures that the silicon–chlorine bond shall be highly reactive. The lower energy of the silicon–carbon bond than of the carbon–carbon bond promotes greater lability of the former, especially in electrophilic substitutions[4]. Silicon is able to form additional bonds by filling vacant 3*d*-orbitals. In most of its compounds silicon is electronically unsaturated[10,11], because its capacity for coordination is not completely utilised in these compounds.

The above specific structural features of the silicon atom and the bonds it forms with carbon and halogens have a definite effect on the reactivity of organosilicon compounds towards halogens.

III. STABILITY OF THE SILICON–CARBON BOND UNDER CONDITIONS OF HALOGENATION

The halogenation of alkylhalogenosilanes at various temperatures involves not only the compounds undergoing halogenation, an elementary halogen, and a catalyst (usually a metal chloride) but also the hydrogen halide which is liberated. All these factors (halogen, hydrogen halide, catalyst, and temperature), either individually or in combination, are able under certain conditions to cleave the silicon–carbon bond. Before considering the halogenation of organosilicon compounds, therefore, it is advisable to discuss the stability of this bond to the above reagents.

The greater polarity of the silicon–carbon bond and the shielding effect of the silicon atom make this bond thermally more stable than is the carbon–carbon bond.

When halogens act on aliphatic compounds of silicon, the hydrogen atoms of the alkyl group undergo radical replacement by halogen. The rate of cleavage of the silicon–carbon bond by bromine or iodine depends on the structure of the initial silane[12], and is greatly increased in the presence of a catalyst of the aprotic acid type. Thus boiling tetraethylsilane with iodine in the presence of aluminium iodide splits off two ethyl groups with the formation of diethyldi-iodosilane[13]. The action of aluminium chloride on tetraethylsilane in chloroform splits off all four ethyl radicals even under ordinary conditions. Iron(III) chloride, bismuth chloride, and mercury(II) chloride also detach aliphatic radicals from the silicon atom under considerably more severe conditions[14]. Tetra-alkylsilanes undergo fission in the presence of aluminium chloride[15].

The introduction of halogen atoms into the alkyl group of an organosilicon compound facilitates its detachment from the silicon atom, the stability of the silicon–carbon bond depending on the position of the halogen relative to the silicon atom[6,8]. α-Halogenoalkylsilanes are relatively stable, with the exception of chloromethyltrialkylsilanes. The introduction of a halogen atom into an aliphatic radical in the β-position with respect to silicon produces a sharp decrease in the stability of the silicon–carbon bond. A γ-halogen atom weakens the bond to a lesser extent than does a β-halogen.

Mono- and di-chloromethyl derivatives of silanes are stable towards acids[16], but in the presence of alkalis quantitative elimination of α-chlorinated alkyl groups takes place. As was to be expected, the polarity and hence the sensitivity of the silicon–carbon bond to nucleophilic reagents falls in the sequence $CCl_3 > CHCl_2 > CH_2Cl$.[17–19] The stability of the silicon–carbon bond improves with increase in the length of the aliphatic chain containing halogen in the α-position to the silicon atom[20], but when a β-halogen atom is present these compounds, on treatment with acids and alkalis, also readily undergo the so called β-decomposition with formation of an alkene[21–25]. The tendency of the molecule to β-decomposition increases markedly with increase in the number of alkyl radicals attached to the silicon atom, and completely substituted derivatives, e. g. $(C_2H_5)_3SiCH_2CH_2Cl$, decompose even on distillation (at 80°C). γ-Decomposition, with the formation of cyclopropane (or propene) and its derivatives, takes place similarly to β-decomposition, but less vigorously.

Halogens and hydrogen halides are able to detach aryl radicals from the silicon atom with the formation of a silicon–halogen bond. Thus the phenyl groups in tetraphenylsilane are eliminated by the action of bromine[26–28]. The removal of an aromatic group by bromine and iodine becomes easier with the accumulation of alkyl radicals on the silicon atom[29,30]. Under more severe conditions (270–300°C) dry chlorine is also able to split off phenyl radicals[31,32]. The stability of the $Si-C_{Ar}$ bond is greatly affected by the nature of other atoms and groups attached to the silicon. Electronegative substituents make cleavage of the bond more difficult, as is shown especially clearly by phenyltrichlorosilane, which can be chlorinated normally by an electrophilic mechanism[32]. Depending on the nature of the substituents the stability of aromatic silicon compounds towards the action of bromine in solvent solution[33] diminishes in the sequence

$$o\text{-}NO_2C_6H_4Si(CH_3)_3 > p\text{-}NO_2C_6H_4Si(CH_3)_3 > m\text{-}NO_2C_6H_4Si(CH_3)_3 > C_6H_5Si(CH_3)_3$$

The products of this reaction indicate that the usual electrophilic replacement of the trimethylsilyl group by bromine has taken place[34]:

$$C_6H_5Si(CH_3)_3 + Br_2 \rightarrow C_6H_5Br + (CH_3)_3SiBr$$

Hydrogen halides act similarly to halogens on the $Si-C_{Ar}$ bond. Comparison of the stability of the aromatic silanes to acid reagents[16–18,35–79] has provided quantitative estimates, based on the Hammett constants δ, of the influence of nuclear substituents on the stability of $Si-C_{Ar}$ bond. It was found that the strength of the bond increases with increase in δ. Nuclear substituents having $\delta > +0.4$ (*m*-CN, *p*-CN, *m*-NO_2, *p*-COOH, *p*-CH_3CO) so strengthen the bond that it is not cleaved by electrophilic reagents[37].

Among the strongest electrophilic reagents are aluminium chloride, iron(III) chloride, and other metal chlorides normally employed as catalysts in the halogenation of aromatic silicon compounds. Aluminium chloride vigorously cleaves the $Si-C_{Ar}$ bond in diphenyldichlorosilane[53], tetraphenylsilane[54], phenyltriethylsilane[55], phenyltrichlorosilane[56–58], and also several other phenyl- and halogenophenyl-silanes[54,56,57,59]. The action of aluminium chloride is especially clearly developed in certain solvents: e.g. in chloroform aluminium chloride cleaves not only the $Si-C_{Ar}$ bond but also the Si–Si, Si–O–Si, and $Si-CH_2C_6H_5$ bonds[53]. It was assumed originally[53–58] that reaction between aromatic silanes and aluminium chloride involves the intermediate formation of phenylaluminium dichloride. Later investigations have shown[60,61] that the true cleaving agent is the acid $HAlCl_4$, formed from aluminium chloride and hydrogen chloride, the latter resulting from the hydrolysis of chlorosilane and aluminium chloride by moist air. In the absence of moisture (or hydrogen chloride) aluminium chloride is unable to effect the cleavage

of phenylchlorosilanes. Yet fission of the Si–C_{Ar} bond in the presence of aluminium chloride is appreciably accelerated by passing hydrogen chloride through the reaction mass[62]. Chlorides of other metals, e.g. iron and antimony, have a more moderate effect on the Si–C_{Ar} bond[58,63-65]. Phosphorus pentachloride is a strong electrophilic reagent, rupturing the silicon–carbon bond in aliphatic and aromatic silanes[27,46].

In contrast to alkylchlorosilanes the introduction of a halogen atom into a phenyl radical produces only a slight increase in polarity of the Si–C_{Ar} bond. In this case the bond is stabilised, as is confirmed by the resistance to alkaline hydrolysis of chlorophenyltrichlorosilane and ethylchlorophenyldichlorosilane[80]. Increasing the number of chlorine atoms in the phenyl group has hardly any effect on the Si–C_{Ar} bond.

IV. RADICAL HALOGENATION (CHLORINATION, BROMINATION) OF SILICON-CONTAINING ALIPHATIC COMPOUNDS

1. Preparation of Chloroalkyl Compounds of Silicon

Chlorination of alkylchlorosilanes in liquid and vapour phases takes place by a radical–chain mechanism. Chlorine and sulphuryl chloride are usually employed as chlorinating agents. Chlorination is initiated by ultraviolet radiation, ionising radiations, peroxides, and other chemical initiators.

(*a*) Chlorination by chlorine

Systematic investigation of the chlorination of aliphatic organosilicon compounds began in 1945, when the photochemical liquid-phase chlorination of several methylchlorosilanes was first achieved[16], after which study of this reaction was continued on a wide scale[17,18,67-76]. Several regularities were found in the chlorination of these compounds. The rate of chlorination of methylchlorosilanes decreases in the sequence

$$(CH_3)_4Si > (CH_3)_3SiCl > (CH_3)_2SiCl_2 > CH_3SiCl_3$$

When one chlorine atom in dimethyldichlorosilane is replaced by a methyl group, the rate of chlorination is increased ninefold[67], which is probably explained by the difference between the induction effects of chlorine atoms and of methyl groups.

In the chlorination of methylchlorosilanes the chlorine exhibits a tendency to replace successively hydrogen atoms in the same methyl group, which indicates that the chloromethyl group is more rapidly chlorinated than is an unsubstituted methyl group. As a consequence, only trichloromethyltrichlorosilane can be obtained by the photochemical liquid-phase chlorination of methyltrichlorosilane[17,68,69,77]. Increase in the number of methyl groups attached to silicon increases the possibility that a second chlorine atom will enter an adjacent methyl group. Thus the chlorination of dimethyldichlorosilane involves the successive replacement by chlorine of the hydrogen atoms only in one methyl group; trimethylchlorosilane yields an appreciable quantity of methylbischloromethylchlorosilane; and the main product of the chlorination of chloromethyltrimethylsilane is bischloromethyldimethylsilane[97,78]. Thus chlorosilyl groups possess a well developed orienting effect[67,73].

It is interesting to compare the chlorination behaviour of methylchlorosilanes and their carbon analogues[67]. Neopentane and tetramethylsilane react readily with chlorine on ultraviolet irradiation[11] to form analogous products, as is evident from the ratios

$$\frac{(CH_3)_3SiCHCl_2}{(CH_3)_3Si(CH_2Cl)_2}=0.66 \qquad \frac{(CH_3)_3CCHCl_2}{(CH_3)_2C(CH_2Cl)_2}=0.67$$

No such analogy is found in the chlorination of trimethylchlorosilane and t-butyl chloride. In an equimolar mixture of these compounds the former is chlorinated more slowly and with preferential substitution by chlorine of hydrogen atoms in the same methyl group, as is evident from the proportions of the chlorination products

$$\frac{(CH_3)_2(CHCl_2)SiCl}{CH_3(CH_2Cl)_2SiCl}=4.9 \qquad \frac{(CH_3)_2(CHCl_2)CCl}{CH_3(CH_2Cl)_2CCl}=0.67$$

These results show that differences in the direction of chlorination are determined primarily by the nature of the central atom.

The marked difference in rates of chlorination between methyl and chloromethyl groups attached to a silicon atom makes it difficult to obtain monochloro-derivatives of methylchlorosilanes, especially chloromethyltrichlorosilane. To obtain an appreciable yield of these compounds the chlorination of methylchlorosilanes is usually conducted at very low degrees of conversion of the initial silane[79]. A high yield of monochloro-derivatives can be achieved by continuous removal of the products from the reaction zone[73,81-89]. This principle has been used in the liquid-phase photochlorination of methylchlorosilanes[90,91] and in obtaining poly(monochloromethyl)silanes[92].

Elementary fluorine has been used[93,94] as initiator for the chlorination of methylchlorosilanes. The mechanism assumed for the reaction is

$$(CH_3)_2SiCl_2 + F_2 \rightarrow CH_3(\dot{C}H_2)SiCl_2 + HF + F\cdot$$
$$(CH_3)_2SiCl_2 + F\cdot \rightarrow CH_3(\dot{C}H_2)SiCl_2 + HF$$
$$CH_3(\dot{C}H_2)SiCl_2 + Cl_2 \rightarrow CH_3(CH_2Cl)SiCl_2 + Cl\cdot, \text{ etc.}$$

Azoisobutyronitrile, which readily generates free radicals when heated above 60°C, has recently become widely used as an initiator for the practical chlorination of organic compounds. Chlorination can be effected with 0.05–0.1% of this initiator in the dark at 70–90°C. Under these conditions the initiator dissociates into $\cdot C(CH_3)_2CN$ radicals, which react easily with chlorine. It is important to note that this compound is widely used in industry at the present time for processes taking place by a radical–chain mechanism. Its use has eliminated the defects inherent in photochemical chlorination (difficulty of producing powerful reaction vessels, danger of fire and explosions, etc.).

The initiated chlorination of organosilicon compounds by elementary chlorine in the presence of azoisobutyronitrile was first proposed in 1956,[95] and has now found practical application for the production of monochloro-derivatives of methylchlorosilanes. This is conducted in the liquid phase at 55–70°C, the content of the initiator in the original silane being initially not more than 0.1%. Subsequently the initiator is added periodically to the reaction mixture, or it is introduced continuously into the latter as a solution in the initial silane.

Chlorination of methylchlorosilanes in the presence of azoisobutyronitrile proceeds in conformity with the usual scheme for a chain reaction:

$$NC(CH_3)_2CN{=}NC(CH_3)_2CN \xrightarrow{\Delta} 2(CH_3)_2\dot{C}CN + N_2$$
$$(CH_3)_2\dot{C}CN + Cl_2 \rightarrow Cl\cdot + (CH_3)_2C(Cl)CN$$
$$CH_3(CH_3)_{3-n}SiCl_n + Cl\cdot \rightarrow \dot{C}H_2(CH_3)_{3-n}SiCl_n + HCl \quad (n=1-3)$$
$$\dot{C}H_2(CH_3)_{3-n}SiCl_n + Cl_2 \rightarrow CH_2Cl(CH_3)_{3-n}SiCl_n + Cl\cdot$$

Depending on the molar proportions of the reactants—the silane and chlorine—it is possible in this way to obtain a wide range of derivatives of methyltrichlorosilane, dimethyldichlorosilane, and trimethylchlorosilane containing chlorine atoms in the methyl groups[96-100]. The main rules of the substitution of hydrogen by chlorine atoms in methylchlorosilanes when chlorinated in the presence of azoisobutyronitrile proved to be the same as for photochemical chlorination. Figs. 1–3 illustrate the dependence of the composition of the chlorination products on the molar ratio of the reactants. The results show the detailed effect of the chlorosilyl group on the direction of the chlorination of methylchlorosilanes, and enable optimum conditions to be selected for obtaining their monochloro-derivatives. It is interesting that the content of monochloro-derivatives in the reaction mixture remains almost constant (at 9–10% for chloromethyltrichlorosilane, and 26–30% for methylchloromethyldichlorosilane and chloromethyldimethylchlorosilane) within a certain range (1 : 0.2–1.0) of molar ratios of silane to chlorine.

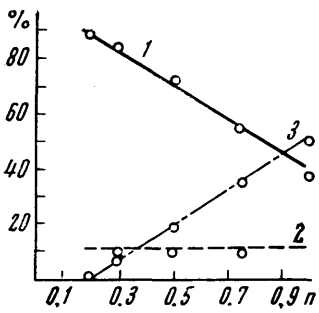


Figure 1. Dependence of composition of chlorination products of methyltrichlorosilane on number n of moles of chlorine per mole of the silane: 1) methyltrichlorosilane; 2) chloromethyltrichlorosilane; 3) dichloromethyltrichlorosilane.

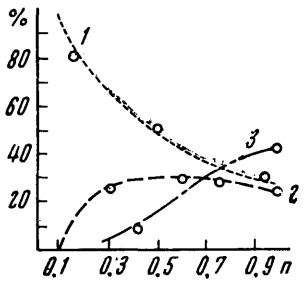


Figure 2. Dependence of composition of chlorination products of dimethyldichlorosilane on number n of moles of chlorine per mole of the silane: 1) dimethyldichlorosilane; 2) methylchloromethyldichlorosilane; 3) dichloro-derivative.

A detailed investigation of the chlorination of methyltrichlorosilane and dimethyldichlorosilane has shown that the composition of the reaction products depends not only

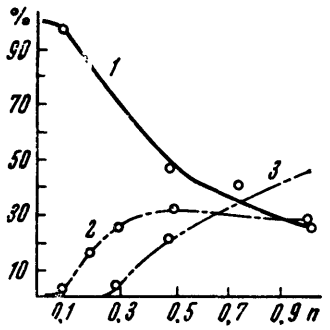


Figure 3. Dependence of composition of products of the chlorination of trimethylchlorosilane on number n of moles of chlorine per mole of the silane: 1) trimethylchlorosilane; 2) chloromethyldimethylchlorosilane; 3) dichloro-derivative.

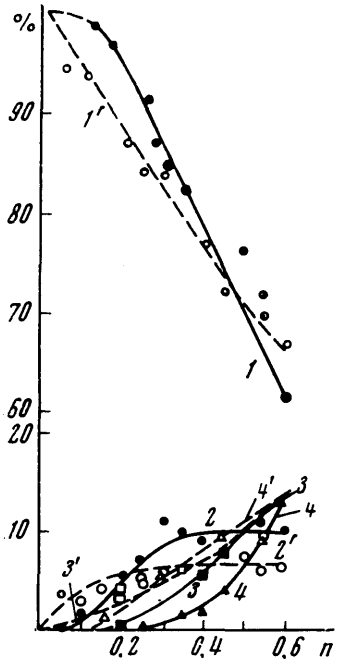


Figure 4. Dependence of composition of products of the chlorination of methyltrichlorosilane on number n of moles of chlorine per mole of the silane for chlorination in the dark in the presence of azoisobutyronitrile (full lines) and during exposure to ultraviolet radiation (broken lines): 1), 1′) methyltrichlorosilane; 2), 2′) chloromethyltrichlorosilane; 3), 3′) dichloromethyltrichlorosilane; 4), 4′) trichloromethyltrichlorosilane.

on the molar proportions of the reactants but also on the nature of the initiator[101] (Figs. 4 and 5). With azoisobutyronitrile as initiator the content of monochloro-derivative in the reaction mixture is 40–70% higher than in photochemical chlorination. It is interesting that, whereas in photochemical chlorination polychloro-derivatives of methyltrichlorosilane are formed at the molar

ratio $CH_3SiCl_3 : Cl_2 = 1 : 0.05$, this occurs with azoisobutyronitrile at a corresponding ratio of 1 : 0.15–0.2. The composition of the polychloro-derivatives is also different in the two cases: whereas in photochemical chlorination trichloromethyltrichlorosilane is formed (1–2%) at the molar ratio $CH_3SiCl_3 : Cl_2 = 1 : 0.15$, when azoisobutyronitrile is used the trichloro-derivative appears in the reaction mixture only at a molar ratio of the reactants of 1 : 0.25, and in only one-sixth of the quantity (0.2%) obtained with photochemical chlorination. Even with the same degree of conversion of the initial silane the quantity of polychloro-derivatives formed per unit weight of the monochloride in the presence of azoisobutyronitrile is 40–70% of the amount obtained in photochemical chlorination (Figs. 6 and 7). Thus the photochemical chlorination of methylchlorosilanes by elementary chlorine is a less selective process than chlorination initiated by azoisobutyronitrile.

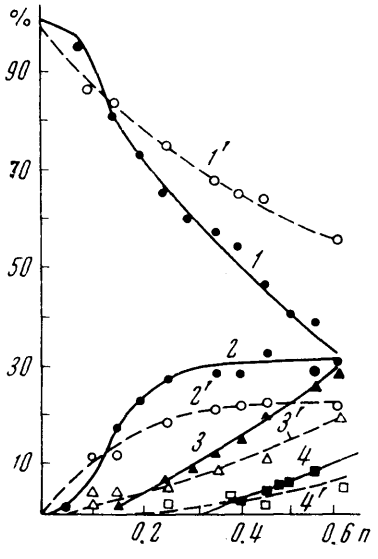


Figure 5. Dependence of composition of products of the chlorination of dimethyldichlorosilane on number *n* of moles of chlorine per mole of the silane for chlorination in the dark in the presence of azoisobutyronitrile (full lines) and during ultraviolet exposure (broken lines): 1), 1′) dimethyldichlorosilane; 2), 2′) methylchloromethyldichlorosilane; 3), 3′) dichloro-derivative; 4), 4′) trichloro-derivative.

The continuous chlorination of methylchlorosilanes in the presence of azoisobutyronitrile has been described[98]. In order to obtain an equivalent yield of the monochloro-derivative the process must be conducted at a lower degree of conversion of the initial silane than in the batch process (e.g. for methyltrichlorosilane 3–4% instead of 10%). The degree of conversion can be increased appreciably by the continuous chlorination of the residue of the initial silane directly in a fractionating column packed with Raschig rings[102]. Methylchlorosilane containing 2–2.5% of the initiator is fed to the upper part of the column, and chlorine gas enters the middle portion. The chlorination products are led from the reaction zone into the lower part of the column, where they are separated from unchanged methylchlorosilane. The latter returns to the reaction zone, where it mixes with the initiator solution supplied to this point. The products collect in the still. This procedure is possible only when a chemical initiator, e.g. azoisobutyronitrile, is used, but cannot be applied to photochemical initiation, since the packing would cut off the action of the light. Under these conditions the conversion of methyltrichlorosilane and dimethyldichlorosilane reaches 70–80% with a yield of monochloro-derivatives of 70–75% (based on the silane used).

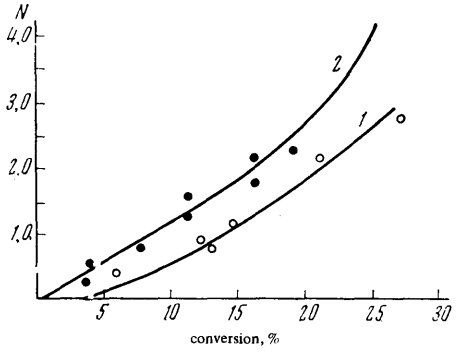


Figure 6. Dependence of quantity *N* of polychlorinated derivatives of methyltrichlorosilane formed per unit weight of the monochloro-derivative on degree of conversion of initial silane for chlorination: 1) in the presence of azoisobutyronitrile in the dark; 2) on ultraviolet exposure.

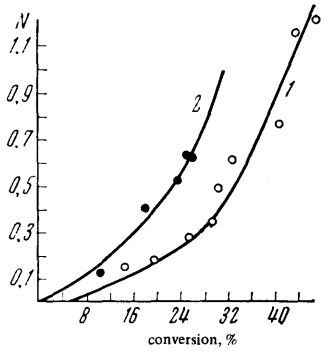


Figure 7. Dependence of quantity *N* of polychlorinated derivatives formed per unit weight of the monochloro-derivative on degree of conversion of dimethyldichlorosilane during chlorination: 1) in the presence of azoisobutyronitrile in the dark; 2) during exposure to ultraviolet radiation.

Another chemical initiator which merits attention is acetyl cyclohexanesulphonyl peroxide[103], which easily decomposes at 30–70°C to form free radicals:

$$C_6H_{11}SO_2OOCOCH_3 \rightarrow C_6H_{11}SO_2O^{\cdot} + CH_3COO^{\cdot}$$

With the chlorination of methyltrichlorosilane and dimethyldichlorosilane as examples this peroxide has been shown to be a more active initiator than is azoisobutyronitrile[104].

Considerably less work has been done on the preparation of polychlorinated methylchlorosilanes and methylpolysiloxanes.

Trichloromethyltrichlorosilane is easily formed by the photochemical chlorination of methyltrichlorosilane in the absence of a solvent at high temperatures[17] or in chloroform under ordinary conditions[68]. The photochemical chlorination of dimethyldichlorosilane extends[68] to the substitution of only five hydrogen atoms, but in the chlorination of trimethylchlorosilane up to eight hydrogen atoms are replaced. Later investigations have confirmed[105,106] that the chlorination of dimethyldichlorosilane in the presence of azoisobutyronitrile proceeds easily to the trichloro-derivative, after which the process is abruptly retarded. Pentachlorodimethyldichlorosilane is formed with great difficulty, requiring the prolonged action of excess of chlorine at 105–110°C. Under these conditions the main process is accompanied by secondary cleavage of the chlorination products at the silicon–carbon bond with the formation of carbon tetrachloride and trichloromethyltrichlorosilane, so that bistrichloromethyldichlorosilane cannot be obtained in this way. Cleavage is greatly diminished by conducting the chlorination of dimethyldichlorosilane under milder conditions—in a solvent (carbon tetrachloride) at 20–25°C (ultraviolet irradiation)—when yields of up to 60% of bistrichloromethyldichlorosilane have been obtained[105,106].

The polychlorination of trimethylchlorosilane is still more difficult[107]. Tristrichloromethylchlorosilane has been obtained in 50% yield only by the prolonged action on trimethylchlorosilane of a large excess of chlorine (molar ratio 19:1) in the presence of azoisobutyronitrile and a small amount of carbon tetrachloride at 53–65°C.

Most polychlorinated methylchlorosilanes are white crystalline substances, sensitive to atmospheric moisture and to heat. Since it is difficult to separate mixtures of these chlorides by distillation, they are converted into alkoxy-derivatives, which can be separated by normal fractional distillation. The following compounds—$CCl_3Si.(OC_2H_5)_3$, $CH_3Si(CCl_3)(OC_2H_5)_2$, $(CCl_3)_2Si(OC_2H_5)_2$, and $(CCl_3)_3SiOC_2H_5$—and also several intermediate chloromethylethoxysilanes—$CH_3Si(CHCl_2)(OC_2H_5)_2$, $CCl_3Si(CH_2Cl).(OC_2H_5)_2$, and $CCl_3Si(CHCl_2)(OC_2H_5)_2$—have been isolated in this way[105,107].

Ethoxytrichloromethylchlorosilanes decompose violently when heated rapidly. Thus trichloromethyltrichlorosilane, in contrast to mono- and di-chloromethyltrichlorosilanes, decomposes readily at 160–175°C:[108]

$$2CCl_3SiCl_3 \rightarrow 2SiCl_4 + C_2Cl_4$$

Tristrichloromethylchlorosilane and ethoxytristrichloromethylsilane are stable when heated, but replacement of a chlorine atom by hydrogen even in only one trichloromethyl group sharply lowers the stability of such a molecule[109]. The exhaustive chlorination of polychloromethylchlorosilanes in a fluidised bed of catalyst (activated carbon) at 300°C results in high yields of carbon tetrachloride and silicon tetrachloride[110].

The polychlorination of linear and cyclic methylsiloxanes exposed to ultraviolet radiation[16,109,111–113] is accompanied by cleavage of Si–O–Si bonds, with the formation of compounds of low molecular weight containing Si–Cl as well as Si–O bonds.

The chlorination of a dimethylsiloxane elastomer as a 5% solution in carbon tetrachloride in the presence of azoisobutyronitrile at 50°C proceeds slowly to the formation of a polymer of mean composition $[(C_2H_2Cl_4)SiO]_n$ and is accompanied by degradation of the molecule[114]. On storage the chlorinated polymer gradually decomposes. Analysis shows that the elastomer chain contains all possible chloromethyl groups—CH_2Cl, $CHCl_2$, and CCl_3—which indicates that it is impossible to obtain a perchlorodimethylsiloxane polymer whose macromolecules are built up solely of $(CCl_3)_2SiO$ units.

In contrast to the dimethylsiloxane elastomer, octamethylcyclotetrasiloxane is chlorinated in the presence of azoisobutyronitrile (at 60°C) without cleavage of Si–O–Si bonds[115], a complicated mixture of chlorides of various degrees of substitution being formed. Chloromethylheptamethylcyclotetrasiloxane has been isolated from the products of the photochemical chlorination of octamethylcyclotetrasiloxane[70,116]. The chlorination of hexamethyldisiloxane is not accompanied by fission of the siloxane bond when the products are able to escape from the reaction zone, so that the yield of monochloro-derivative is quite high[86,117]. Under analogous conditions methoxytrichlorosilane gives $ClCH_2OSiCl_3$, exhaustive chlorination of which yields CCl_3OSiCl_3.[119,120] The products of the photochemical chlorination of methylchlorodisilanes

$$(CH_3)_n Cl_{3-n} SiSiCl_{3-m} (CH_3)_m \; (n\,m = 0, 1, 2;\; n+m>1)$$

at 0–100°C are $(ClCH_2)(CH_3)_{n-1}Si_2Cl_{6-n}$.[121]

Perchlorinated methylchlorosilanes and methylsiloxanes may decompose spontaneously and explosively[109].

The chlorination of the higher alkylchlorosilanes exhibits special features due to the nature of the alkyl radicals.

Ethyl derivatives of silicon react readily with chlorine. Tetraethylsilane is chlorinated under normal conditions in the absence of initiators with the formation of mono- and di-chloro-derivatives[122,123], the reaction being accelerated appreciably by the addition of phosphorus pentachloride[20,22,124]. Study of the photochemical chlorination of ethylchlorosilanes[73,125–129] has established certain rules for the direction of chlorination. In effect only hydrogen attached to an α-carbon atom in tetraethylsilane is replaced by chlorine. The activity of hydrogen atoms attached to a β-carbon atom increases appreciably with the accumulation of chlorine atoms attached to silicon in ethylchlorosilanes; thus the monochloro-derivative formed by the chlorination of ethyltrichlorosilane contains a considerable quantity of the β-chloride ($CH_3CHClSiCl_3 : ClCH_2CH_2SiCl_3 = 1 : 1.6–1.8$). The chlorination of ethylchlorosilanes in the presence of azoisobutyronitrile[130] maintains essentially the same effects of silyl groups on the rate and the direction of chlorination as in the photochemical process. The yields of monochloro-derivatives of ethylchlorosilanes are equivalent in the two cases, but the simplicity of the apparatus required indicates that preference should be given to chlorination initiated by azoisobutyronitrile.

The polychlorination of ethyltrichlorosilane and diethyldichlorosilane in the presence of azoisobutyronitrile (at 80°C), and also on ultraviolet irradiation[130–133], in contrast to the corresponding chlorination of methylchlorosilanes, does not involve fission of the silicon–carbon bond and leads to the formation of the perchloroethyl derivatives [$C_2Cl_5SiCl_3$ and $(C_2Cl_5)_2SiCl_2$]. Under these conditions tetrachloroethyltrichlorosilane has been isolated from the products of the polychlorination of ethyltrichlorosilane. The hydrolysis of polychloroethylchlorosilanes with water and aqueous alkalis is accompanied by β-decomposition with the formation of tetra- and tri-chloroethyl-

enes. The dehydrochlorination of tetrachloroethyltrichlorosilane under the influence of high temperatures and also of quinoline[131] involves β-decomposition; the main product of dehydrochlorination under the influence of aluminium chloride is trichlorovinyltrichlorosilane. This compound is formed also by the dechlorination of perchloroethyltrichlorosilane in the presence of copper powder[131].

A β-orienting effect is still more strongly developed with ethylfluorosilanes ($CH_3CHClSiF_3$: $ClCH_2CH_2SiF_3$ = 1 : 4.4),[134] which is explained by the considerably greater electronegativity of the fluorine than of the chlorine atom. It is interesting that, when ethylmethyldichlorosilane undergoes chlorination, the chlorine enters mainly the ethyl radical[135]. Attempts have been made[126,136] to explain the rules of the chlorination of ethylchlorosilanes by the electronic structure of these compounds.

The orienting effect of the trichlorosilyl group is apparent also in the photochemical chlorination of propyltrichlorosilane[87], as is indicated by the relative proportions of 1-, 2-, and 3-chloropropyltrichlorosilanes formed (0.7 : 1 : 1). As with ethyltrichlorosilane, 70% more of the β-chloro-derivative than of the α-chloro-derivative is formed from isopropyltrichlorosilane[137]. These and other papers[138,139] refer to the need to remove monochloro-derivatives from the reaction zone. This method has been used also for the chlorination of bistrichlorosilylmethane[87], 1,2-bistrichlorosilylethane[23,87,140], and several other chloroalkylchlorosilanes[78,92,139,141]. The photochemical chlorination of $CF_3CH_2CH_2SiCl_3$ and $CF_3CH_2CH_2SiCl_2CH_3$ leads to the formation of monochloro-derivatives containing the chlorine atom in the CF_3CH_2CHCl radical mainly in the α-position relative to the silicon atom[142,143]. With $CF_3CH_2CH_2SiCl(CH_3)_2$ and $CF_3CH_2CH_2SiCl_2C_2H_5$ the direction of chlorination is determined not only by the trifluoromethyl group but also by the nature of the chlorosilyl group[144].

The liquid-phase photochemical chlorination of more complicated organosilicon compounds has been described[19,145-149], and also the preparation of polychloro-derivatives of several other alkylchlorosilanes[150-153].

Cobalt-60 γ-radiation has been used to initiate the chlorination of alkylchlorosilanes, in particular trimethylchlorosilane[153,154]. The chlorination of methylchlorosilanes under the influence of radiation[155-158] conforms mainly to the same rules as their chlorination under the influence of ultraviolet radiation and in the presence of chemical initiators. The composition of the products, determined by the molar proportions of the reactants (silane and chlorine), is independent of the dosage rate. The radiation chlorination of a dimethylsiloxane elastomer has been reported[159,160]. The radiation chlorination of ethyltrichlorosilane[157,158] leads to the formation of α- and β-chloro-derivatives in the proportions 1 : 1.7, in agreement with results for the chlorination of ethylchlorosilane on exposure to ultraviolet radiation[73] and in the presence of azoisobutyronitrile[130].

A new method for obtaining chlorinated polyorganosiloxanes proposed recently is based on the combined hydrolytic polycondensation and chlorination of silicon-containing compounds by the hydrolysis of alkylchlorosilanes containing no chlorine atom in the hydrocarbon radicals, with simultaneous introduction of oxidants such as hydrogen peroxide, manganese dioxide, etc. into the reaction[161]. These convert the hydrogen chloride, formed by hydrolysis, into chlorine, which chlorinates the organic radical attached to the silicon. In this case three reactions—hydrolysis, condensation, and chlorination—take place in a single stage, but the apparent simplification in fact does not yield a polymer of high quality, and the technology is greatly complicated by the additional stage of purifying the final product from oxidants. In contrast to known processes of the oxidative chlorination of hydrocarbons, therefore, the above reaction is of no practical interest.

Little information has been published on the vapour-phase chlorination of alkylchlorosilanes at elevated temperatures (in the absence of ultraviolet radiation). Ethylchlorosilane at 350°C yields α- and β-monochloro-derivatives in the ratio 1 : 1.08.[141] When vinyltrichlorosilane is chlorinated under these conditions the main product is CH_2 : $CClSiCl_3$;[162] at a lower temperature (100–200°C) the reaction shifts towards formation of $ClCH_2CHClSiCl_3$. The chlorination of $F_2CHCF_2SiCl_3$ (at 150–200°C) yields $ClCF_2CF_2SiCl_3$.[163]

Unsaturated organosilicon compounds are chlorinated extremely readily by elementary chlorine to form predominantly addition products[69,77,162-169]. In contrast to vinyltrichlorosilane, however, trichlorovinyltrichlorosilane does not add chlorine at the double bond in the absence of illumination at 0–100°C.[170,171] The presence of lithium chloride under these conditions accelerates the addition of chlorine. Ultraviolet irradiation produces an especially marked acceleration of the reaction, its mechanism changing from heterolytic to a chain (homolytic) mechanism. The presence of an electron-donor trimethylsilyl group in the vicinity of the double bond in the trichlorovinyl radical facilitates the addition of chlorine to the double bond: thus trimethyltrichlorovinylsilane readily adds chlorine at the double bond in the absence of irradiation at 20°C.

(*b*) Chlorination by sulphuryl chloride

Chlorination by sulphuryl chloride is usually accomplished in the presence of the free-radical type of initiators. With methylchlorosilanes this method of chlorination initially gave negative results[21,172,173]. Subsequently the use of chlorobenzene as medium enabled the temperature of the reaction to be raised and this accelerated the decomposition of benzoyl peroxide into the free radicals necessary for the occurrence of chlorination. In this way sulphuryl chloride can be used to chlorinate trimethylchlorosilane[173] and other methylchlorosilanes[69,174]. Under these conditions it is comparatively easy to chlorinate also bistrichlorosilylmethane and 1,2-bistrichlorosilylethane in spite of the presence of two trichlorosilyl groups[87]. In bistrimethylsilylmethane the methyl groups are the first to be chlorinated[175]. There are references to the chlorination with sulphuryl chloride of other silicon compounds containing a methyl group and a methylene group[21,176-179]. The chlorination of alkylchlorosilanes with sulphuryl chloride during exposure to ultraviolet radiation[180,181] enables individual chloro-derivatives of different degrees of substitution to be obtained depending on the molar ratio of the reactants. Such selectivity is not observed when chlorine is used.

The chlorination of methylchlorosilanes with sulphuryl chloride can be initiated by azoisobutyronitrile[182], which decomposes into free radicals at a lower temperature than is observed with benzoyl peroxide.

Ethylchlorosilanes are readily chlorinated by sulphuryl chloride in the absence of solvents, when 1- and 2-chloroethylchlorosilanes are formed[21,82,183]. Chlorine enters ethylmethyldichlorosilane predominantly in the ethyl group[184]. The chlorination of tetraethylsilane yields only

the α-isomer[22,73,84,185]. With decrease in the number of ethyl radicals attached to the silicon atom the β-orienting effect of the trichlorosilyl group is more strongly developed when sulphuryl chloride is used than on chlorination with chlorine[21,77,125,183,186]. For example, the proportions of 1- and 2-chloroethyltrichlorosilanes obtained with sulphuryl chloride are 1:2.5, compared with the 1:1.6–1.8 with chlorine.

The directional effect of a chlorosilyl group is evident also in the chlorination of higher alkylchlorosilanes by means of sulphuryl chloride[24,188,189]. Several cyclic organosilicon compounds react effectively with sulphuryl chloride[190–193]. The above regularities are observed also in the chlorination of alkylchlorosilanes containing chlorine atoms in the alkyl group, although the orienting effect of the trichlorosilyl group is then more complicated. Thus 2-chloroethyltrichlorosilane yields only the 2,2-derivative, whereas 1-chloroethyltrichlorosilane forms equal proportions of 1,1- and 1,2-dichloroethyltrichlorosilanes.

(*c*) Chlorination by *t*-butyl hypochlorite

t-Butyl hypochlorite can be used to chlorinate alkylchlorosilanes and alkylpolysiloxanes, the reaction being initiated with peroxides and ultraviolet radiation. Compounds of the types $(R_3Si)_2O$ (R = CH_3), $(R_2SiO)_4$, $C_6H_5SiR_3$, R_3SiCH_2Cl, R_4Si, and $(R_3Si)_2$ can be chlorinated by means of this agent[194,195]. However, this method is of no practical interest because of the difficulties of manipulations with t-butyl hypochlorite, resulting from the violent decomposition of the latter under the influence of light, heat, or contact with rubber.

2. Preparation of Bromoalkyl Compounds of Silicon

In contrast to chlorine, bromine does not always react with alkylchlorosilanes. It reacts extraordinarily easily with hydrocarbon derivatives of silicon[196–201], especially with the higher tetra-alkylsilanes[196,197]. As with chlorination, bromine first enters an α-position in tetraethylsilane[143,196–199]. A similar situation is found in the bromination of $(iso\text{-}C_3H_7SiO_{1.5})_8$ by means of *N*-bromosuccinimide[202].

Bromination of methyl- and ethyl-chlorosilanes has proved possible only by the combined action of bromine, chlorine, and ultraviolet radiation[179,183,203–206]. Sulphuryl chloride can be used instead of chlorine[207].

The photochemical bromination of linear and cyclic methylsiloxanes with a mixture of bromine and chlorine leads to the formation of mono- and poly-brominated derivatives[200,203,208,209]. Incompletely methylated polysiloxanes have been selectively brominated with bromine in the presence of a stoichiometric quantity of pyridine[210].

Bromine is easily added at the double bonds in unsaturated organosilicon compounds[167,211,212]; under certain conditions substitutive bromination is possible[213]. The bromination of allyltriethylsilane[25] and allyltrimethylsilane[214] is accompanied by β-decomposition of the reaction products. Allyldiethylsilane, naphthyltriallylsilane, and vinyltriethylsilane add bromine without cleavage of the silicon–carbon bond[25]. Trichlorovinyltrichlorosilane, unlike vinyltrichlorosilane, does not add bromine at 20–80°C.[171] Nor does trichlorovinyltrimethylsilane react with bromine at 20°C, although it readily adds chlorine under these conditions, as mentioned above. When the temperature of the reaction is raised to 80–85°C products resulting from cleavage at the silicon–carbon bond—bromotrichloroethylene and trimethylbromosilane—are formed exclusively[171].

V. ELECTROPHILIC HALOGENATION (CHLORINATION, BROMINATION) OF SILICON-CONTAINING AROMATIC AND ALIPHATIC–AROMATIC COMPOUNDS

Systematic study of the direct halogenation of aromatic and aliphatic–aromatic compounds of silicon began in 1948 with the catalytic chlorination of phenylchlorosilanes. Earlier work had been concerned mainly with the preparation of monohalogeno-derivatives of certain aromatic silanes by the organomagnesium method[215,216]. The direct halogenation of aromatic compounds of silicon is an electrophilic substitution catalysed by metal halides. This reaction easily leads to the substitution by halogen of the hydrogen atoms in the aromatic ring.

1. Preparation of Chloroaryl Compounds of Silicon

The first mention of the direct chlorination of phenyltriethylsilane appeared in 1874.[217,218] In 1941 the patent literature reported the possibility of obtaining polychlorophenylchlorosilanes by chlorinating diphenyldichlorosilane and methylphenyldichlorosilane with chlorine in the presence of iron and antimony halides as catalysts at 70 to 120°C.[219] Later investigations of the electrophilic chlorination of aromatic silanes established that, in the presence of iron, iron(III) chloride[220], antimony(III) chloride[25,222], aluminium chloride[221], iodine, or phosphorus pentachloride[222], different numbers of chlorine atoms can be introduced into the phenyltrichlorosilane[223–225] and diphenyldichlorosilane[224] molecules depending on the molar ratio of the reactants and the temperature. In the absence of a catalyst this reaction does not take place even at high temperatures (150–200°C). The electrophilic chlorination of phenyltrichlorosilane and diphenyldichlorosilane has been described also in several other publications[80,226–233].

Depending on the conditions—the presence of a catalyst and its nature, the duration of the action of chlorine, and the temperature—the substitutive chlorination of phenylchlorosilanes is accompanied by the parallel cleavage of the $Si-C_{Ar}$ bond[32,224,234]. This side-reaction occurs only in the presence of catalysts—metal halides—which form the sequence $AlCl_3 > FeCl_3 \gg SbCl_5$ according to their dearylating activity, in conformity with which this reaction occurs more or less intensely[57,58]. Cleavage of the $Si-C_{Ar}$ bond can be diminished by conducting chlorination at a lower temperature and in a solvent[235]. As already stated above, hydrogen chloride must be present in the reaction mixture for phenylchlorosilanes to be cleaved by metal halides (e.g. aluminium chloride)[60,61]. The chlorination of phenylchlorosilanes in the presence of iodine is not accompanied by rupture of the $Si-C_{Ar}$ bond.

The reactivity of arylchlorosilanes in electrophilic halogenation is determined by the nature of the atoms and groups attached to the silicon atom. In recent years various aromatic compounds containing a silyl group in the benzene ring or in a side-chain have been subjected to electrophilic halogenation. The results have provided a more exact idea of the orienting influence of the silyl group and have revealed the reactivity of several arylsilanes and alkylarylsilanes towards electrophilic substitution as a function of the nature of the atoms and groups attached to silicon.

The *meta*-orienting nature of the trichlorosilyl group, which is a consequence of its electron-acceptor properties, is clearly evident in the fact that the benzene ring in phenyltrichlorosilane is so deactivated that it does not react with either chlorine[224] or bromine[236] at 150–200°C, in contrast to benzene itself, which with bromine is able to give phenyl bromide in the absence of catalysts even at 60°C.[237] This *meta*-orienting power is distinctly shown also in the electrophilic chlorination of phenyltrichlorosilane, which gives a mixture of the *meta*-, *ortho*-, and *para*-isomers in the proportions 75 : 21 : 4 [238] and 74 : 24 : 2.[226] The trifluorosilyl group had a still stronger *meta*-orienting effect under these conditions (82 : 18 : 0).[239] Further investigations have shown[240] that on electrophilic chlorination phenyltrifluorosilane is more subject than phenyltrichlorosilane to cleavage at the silicon–carbon bond, so that only mono- and di-chloro-derivatives of phenyltrifluorosilane can be isolated from the reaction products.

It must be emphasised that, despite the deactivation of the aromatic ring in phenyltrichlorosilane, it can be chlorinated with chlorine in the presence of ionic catalysts even below 0°C with the formation solely of substitution products, in which the *meta*-isomer predominates[241]. A similar effect of the trichlorosilyl group is evident in the chlorination of phenyltrichlorosilane by means of iodine trichloride[242]. As a consequence of the presence of strongly polarised chlorine in this latter agent, the reaction takes place readily even at −40°C with the formation of a mixture of mono- and di-chloro-derivatives. Rise in temperature to −20°C appreciably accelerates the reaction, and under these conditions chlorination is accompanied by partial iodination of the aromatic ring. At 20°C the reaction occurs violently with the evolution of elementary iodine and the formation of substituted mono-, di-, and tri-chloro-derivatives. Unlike iodine trichloride the monochloride does not react with phenyltrichlorosilane at 20°C.[242]

With rise in temperature to 200°C the *meta*-orienting effect of the trichlorosilyl group on the chlorination of phenyltrichlorosilane becomes weaker (*meta* : *para* : *ortho* = 60 : 15 : 25).[243] At 350–400°C the trichlorosilyl group loses its *meta*-orienting power (39 : 39 : 22).[244]

The chlorination of phenyltrichlorosilane by means of sulphuryl chloride exposed to ultraviolet radiation[181] is extremely sluggish and is accompanied by cleavage of the $Si-C_{Ar}$ bond.

The introduction of an *ortho*–*para*-orienting substituent (methyl) into the phenyltrichlorosilane molecule results in some activation of the aromatic ring, so that *p*-tolyltrichlorosilane, in contrast to phenyltrichlorosilane, reacts with chlorine in the absence of a catalyst at only 95–100°C.[245] In the presence of metal halides [iron(III) chloride, antimony trichloride] *p*-tolyltrichlorosilane is easily chlorinated as far as the replacement of three hydrogen atoms in the aromatic ring. When an attempt is made to obtain the tetrachloro-derivative, cleavage of the $Si-C_{Ar}$ bond takes place. The results obtained for the interaction of a halogen with *p*-tolyltrichlorosilane indicate that the latter behaves normally in electrophilic substitutions: the entering halogen atom is directed by both existing substituents (1-methyl and 4-trichlorosilyl), in conformity with their nature, to position 2.

The introduction, into the aromatic ring of phenyltrichlorosilane, of a second kind of orienting group (trichloromethyl), which is a *meta*-orienting substituent, results in strong deactivation of the benzene ring. In fact, *p*-trichloromethylphenyltrichlorosilane is difficult to chlorinate at 100–110°C even in the presence of catalysts[245], mono- and dichloro-derivatives being formed; further chlorination of this compound results in cleavage of the $Si-C_{Ar}$ bond. A chlorine atom entering the aromatic ring of *p*-trichloromethylphenyltrichlorosilane is directed by both substituents (1-trichloromethyl and 4-trichlorosilyl) to positions 2 and 3.

The trifluoromethyl group has a still stronger deactivating effect on an aromatic ring, so that *p*-trifluoromethylphenyltrichlorosilane and *p*-trifluoromethylphenyltrifluorosilane, in contrast to *p*-trichloromethylphenyltrichlorosilane, do not react with chlorine at 120°C even in the presence of iron(III) chloride[246].

A similar effect is observed when two trichlorosilyl groups are present in the aromatic ring. Electrophilic chlorination of bistrichlorosilylbenzene takes place with great difficulty, and leads to the substitution of only one hydrogen atom in the aromatic ring. Further chlorination results in cleavage of the $Si-C_{Ar}$ bond[247].

The methylene bridge separating the trichlorosilyl group from the aromatic ring in benzyltrichlorosilane produces marked changes in the orienting influence and the deactivating effect of the trichlorosilyl group[248]. Unlike phenyltrichlorosilane, benzyltrichlorosilane reacts with chlorine even at ordinary temperatures to form *p*-chlorobenzyltrichlorosilane. In the presence of catalysts the whole possible range of chloro-derivatives containing 1–5 nuclear chlorine atoms is formed: the first chlorine atom enters the ring only in the *para*-position, and the next two chlorine atoms *ortho* to the trichlorosilylmethyl group[248,249]. In contrast to phenyltrichlorosilane, these reactions are not accompanied by cleavage of the silicon–carbon bond. Similar results have been obtained for the electrophilic chlorination of benzylmethyldichlorosilane: methylpentachlorobenzyldichlorosilane $C_6Cl_5CH_2SiCl_2CH_3$ has been isolated from the products of the reaction[250].

It is interesting that the trichlorosilyldichloromethyl group, in contrast to the trichlorosilylmethyl group, is *meta*-orienting towards a chlorine atom entering the aromatic ring. Thus the electrophilic chlorination [in the presence of iron, iron(III) chloride, antimony(V) chloride] of $\alpha\alpha$-dichlorobenzyltrichlorosilane yields *m*-chlorophenyldichloromethyltrichlorosilane[242]. Further chlorination gives the trichloro-derivative. The compound containing five chlorine atoms in the ring cannot be obtained because of cleavage of the silicon–carbon bond.

The replacement of halogen atoms attached to silicon by the less electronegative alkyl groups leads to a change in the orienting effect of the silyl group. A detailed study of this phenomenon has been made on the electrophilic halogenation of methylphenyldichlorosilane[251–253] and phenyltrimethylsilane[239,254].

The chlorination of phenylmethyldichlorosilane in the absence of catalysts at 50–115°C results in nuclear substitution (to give mono-, di-, and tri-chloro-derivatives) and is accompanied by appreciable cleavage of the $Si-C_{Ar}$ bond. At 145–150°C compounds of the type $C_6H_{5-n}Cl_n \cdot SiCl_2CCl_3$ appear, which under these conditions readily decompose at the $Si-C_{Alk}$ bond to form carbon tetrachloride and $C_6H_{5-n}Cl_nSiCl_3$.[254] The chlorination of phenylmethyldichlorosilane in the presence of antimony trichloride[252,253] leads to the formation merely of the dichloro-derivative and is accompanied by considerable cleavage of the $Si-C_{Ar}$ bond. On chlorination in the presence of iodine[253,256], especially under mild conditions (in carbon tetrachloride at 10–12°C),[253] degradation is greatly diminished, so that trichlorophenylmethyldichlorosilane can be obtained. The yield of polychloro-derivatives is increased by chlorinating in the presence of iodine

the monochloro-derivative, chlorophenylmethyldichlorosilane[257]. The rate of chlorination of the aromatic ring and the rate of cleavage of the $Si-C_{Ar}$ bond increase in the sequence $C_6H_5SiCl_2CH_3 < C_6H_5SiCl(CH_3)_2 < (C_6H_5)_2SiClCH_3$.[256] Phenylmethyldichlorosilane does not react with sulphuryl chloride in the presence of ionic catalysts.

During electrophilic chlorination phenyltrimethylsilane undergoes considerable cleavage at the $Si-C_{Ar}$ bond, so that the yield of the monochloro-derivative does not exceed 50%.[254]

Phenylmethyldichlorosilane yields ~60% of the *m*-chloro-isomer, but chlorination of phenyltrimethylsilane gives mainly the other two isomers (*para* + *ortho* : *meta* = 78 : 22).[239,254] Thus the replacement of chlorine atoms attached to silicon by electropositive methyl radicals changes the *meta*-orienting power of the silyl group into an *ortho*–*para*-orientation effect.

It is interesting that the presence of the trichloromethyl group attached to silicon in phenyltrichloromethyldichlorosilane results in considerable deactivation of the aromatic ring and strengthening of its bond with silicon. In its behaviour towards electrophilic chlorination this compound resembles phenyltrichlorosilane, the trichloromethyldichlorosilyl group, like the trichlorosilyl group, having a *meta*-orienting effect[258]. Phenyltrichloromethyldichlorosilane behaves similarly on electrophilic bromination[259].

The chlorination of 1-naphthyltrichlorosilane[260] in the presence of the usual catalysts for the halogenation of aromatic compounds [iron(III) chloride, antimony trichloride] at 55–100°C yields various chloro-derivatives (from mono- to tetra-chloronaphthyltrichlorosilanes) in yields of 60–90%. Cleavage of the silicon–carbon bond does not occur and, in spite of the prolonged action of excess of chlorine (molar proportions of $1\text{-}C_{10}H_7SiCl_3 : Cl_2 = 1 : 25$), the reaction terminates at the formation merely of the tetrachloro-substituted derivative. Attempts to obtain more highly chlorinated products by raising the temperature (to 150°C and above) have been unsuccessful, since cleavage of the silicon–carbon bond occurs under these conditions.

Several publications have appeared on the ionic chlorination of certain other aromatic silanes—biphenyl-4-yltrichlorosilane[261], *p*-xylyltrichlorosilane[262], and tetraphenylsilane[263]. Polychloro-derivatives of aromatic silanes have been obtained by chlorinating the latter in the presence of a mixed catalyst ($FeCl_3 + SbCl_5$),[229] and also in the presence of aluminium chloride and iron(III) chloride in an organic solvent[238,263]. Chlorination of polytitanophenylsiloxanes[264] and polyaluminophenylsiloxanes[265] in the presence of a catalyst (phosphorus pentachloride) in carbon-tetrachloride solution gives the corresponding polymers having chlorine atoms in the phenyl groups, which possess improved thermal stability in comparison with the original compounds.

2. Preparation of Bromoaryl Compounds of Silicon

With rare exceptions the direct bromination of arylsilanes is accompanied by cleavage of the $Si-C_{Ar}$ bond[27-29,33,215,239]. The tendency for the aromatic ring to become detached from the silicon atom diminishes as chlorine atoms accumulate on the silicon. Thus the bromination of phenyltrichlorosilane in the presence of iron(III) chloride gives a quite high yield of mono- and di-bromo-derivatives[203,224,226,236]. It is interesting that most (69%) of the bromophenyltrichlorosilane formed comprises a mixture of the *p*- and *o*-bromo-isomers (38% and 31%). These results indicate that the trichlorosilyl group exhibits an anomalous *ortho*–*para*-orienting effect during bromination.

Extraordinary ease of detachment is exhibited by the trifluorylsilyl group when phenyltrifluorosilane is brominated in the presence of iron[239]. Under mild conditions of bromination it is possible to obtain monobromophenyltrifluorosilane (in 52% yield)[240], which is a mixture of isomers (*meta* : *para* + *ortho* ≃ 60 : 40).

Phenylmethyldichlorosilane reacts readily with bromine in the absence of catalysts at 0–25°C to form mono- and di-bromophenylmethyldichlorosilanes[266]. Further increase in the extent of bromination under these conditions, as well as bromination in the presence of ionic catalysts, leads to considerable cleavage of the reaction products at the $Si-C_{Ar}$ bond. The first bromine atom to enter the aromatic ring of phenylmethyldichlorosilane occupies predominantly the *ortho* and *para* positions (*meta* : *ortho* : *para* = 25 : 35 : 40).

Phenyltrimethylsilane is cleaved quantitatively by bromine at the $Si-C_{Ar}$ bond, even under mild conditions.

Publication of a series of papers on the direct bromination of phenyltrichlorosilane[236], benzyltrichlorosilane[248], *p*-tolyltrichlorosilane[254], and phenylmethyldichlorosilane[266] has been followed by other investigations in this field. Study of the electrophilic bromination of compounds of the type $C_6H_5[CH_2]_nSiCl_mR_{3-m}$ ($n = 1, 2$; $m = 0-3$; and $R = CH_3$, C_2H_5) showed that in all cases the $[CH_2]_nSiCl_m$·R_{3-m} groups are strongly *ortho*–*para*-orienting[249,267]. The high reactivity of benzyltrimethylsilane compared with benzyltrichlorosilane is explained by conjugation of the silicon–carbon bond with the aromatic ring[267]. The bromination of benzyltrifluorosilane, in contrast to that of phenyltrifluorosilane, is not accompanied by cleavage of the silicon–carbon bond, the sole product being the *p*-bromo-isomer[239].

3. Mechanism of Electrophilic Substitution and Cleavage of the $Si-C_{Ar}$ Bond in Aryl- and Alkylaryl-chlorosilanes

The characteristic features of the substitutive chlorination of aryl- and alkylaryl-chlorosilanes agree well with the generally accepted mechanism of electrophilic substitution in the aromatic series:

$$Cl_2 + MCl_3 \rightleftarrows \overset{\delta+}{Cl} \ldots Cl \ldots \overset{\delta-}{MCl_3} \rightleftarrows \overset{+}{Cl}\,[MCl_4]^-$$

(M = Fe, Al, Sb)

$$C_6H_5SiCl_3 + \overset{+}{Cl}\,[MCl_4]^- \rightarrow \left[\text{C}_6\text{H}_5(\text{SiCl}_3)(\text{Cl})\right]^+ [MCl_4]^- \rightarrow C_6H_4ClSiCl_3 + HCl + MCl_3$$

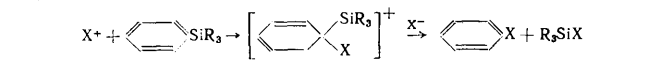
Phenylchlorosilanes react by a similar mechanism with iodine trichloride, which acts here as a reactive electrophilic form of the halogen[242]:

$$ICl_3 \rightleftarrows \overset{+}{Cl}\,[ICl_2]^-$$

$$C_6H_5SiCl_3 + \overset{+}{Cl}\,[ICl_2]^- \rightarrow \left[\text{C}_6\text{H}_5(\text{SiCl}_3)(\text{Cl})\right]^+ [ICl_2]^- \rightarrow C_6H_4ClSiCl_3 + HCl + ICl$$

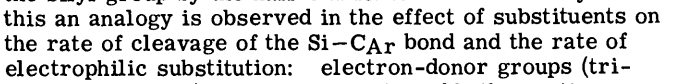
As already noted above, a characteristic feature of the electrophilic halogenation of arylsilanes and alkylarylsilanes is the accompanying secondary degradative halogenation involving cleavage of starting materials and products at the $Si-C_{Ar}$ bond with the formation of halogenated aromatic derivatives not containing silicon. A definite relation exists between such cleavage and electrophilic substitution in aryl- and alkylaryl-chlorosilanes[37-52,69,268-273].

Thus trialkylsilyl groups are detached from an aromatic ring by a mechanism of electrophilic substitution[33,44-51]:



In this case electrophilic attack on the aromatic ring by the halogen cations, leading to formation of an intermediate addition product, is accompanied by nucleophilic attack on the silyl group by the halide anions. In conformity with this an analogy is observed in the effect of substituents on the rate of cleavage of the $Si-C_{Ar}$ bond and the rate of electrophilic substitution: electron-donor groups (trimethylsilyl, etc.) increase the rates of both reactions; electron-acceptor groups (trichlorosilyl) decrease the rates. The tendency of the $Si-C_{Ar}$ bond to undergo cleavage by the halogen falls rapidly in the sequence $C_6H_5Si(CH_3)_3 > C_6H_5SiCl(CH_3)_2 > C_6H_5SiCl_2CH_3 > C_6H_5SiCl_3$. The rate of cleavage is determined not only by the nature of the silyl group but also significantly by induction and steric effects, the nature of the halogen, the catalyst, and other factors.

Cleavage of the $Si-C_{Ar}$ bond by the hydrogen halide formed during halogenation in the presence of ionic catalysts takes place by an analogous mechanism of electrophilic substitution[60-62,239,274]:



where R = Alk, Cl, F; X = Cl, Br; and M = Fe, Al, Sb.

The sequence of increasing stability of aromatic silanes to cleavage by the $HX.MX_3$ complex under conditions of halogenation is

$$R_3'SiR < RR'SiCl_2 < R_2SiCl_2 < RSiF_3 < p\text{-}R'C_6H_4SiCl_3 < p\text{-}CCl_3C_6H_4SiCl_3 < RSiCl_3,\ RSiCl_2(CCl_3),$$

where R = C_6H_5 and R′ = CH_3.

Fluorine atoms, in spite of their greater electronegativity, are for steric reasons incapable of resisting nucleophilic attack on the silicon atom, so that cleavage of the $Si-C_{Ar}$ bond takes place more easily in phenyltrifluorosilane than in phenyltrichlorosilane.

VI. RADICAL HALOGENATION (CHLORINATION, BROMINATION) OF SILICON-CONTAINING ALIPHATIC–AROMATIC AND AROMATIC COMPOUNDS

1. Substitutive Halogenation with Replacement of Alkyl Hydrogen Atoms by Chlorine and Bromine

The photochemical chlorination of alkylarylchlorosilanes yields substitution products containing chlorine in the alkyl radical or in the aliphatic portion of an aralkyl group[179,275-280]. It is interesting that *o*-tolyltrichlorosilane, in contrast to *p*-tolyltrichlorosilane, is not chlorinated, probably because of the steric effect of the trichlorosilyl group[155,277], for the less bulky trifluorosilyl group does not exert such hindrance. Benzyltrichlorosilane can be chlorinated with sulphuryl chloride in the presence of benzoyl peroxide[173].

Tolyl and benzyl groups in hydrocarbon derivatives of silicon are easily brominated by *N*-bromosuccinimide, usually without cleavage of the $Si-C_{Ar}$ bond[179,281,282]. Tetra-*p*-tolylsilane and certain other hydrocarbon derivatives of silicon are exceptions[179,283]. When benzylsilane is brominated in weak daylight (at 8°C), α-bromobenzyltribromosilane is formed. Heating a mixture of benzylsilane and bromine in sunlight yields αα-dibromobenzyltribromosilane[284].

The radical chlorination of aliphatic–aromatic chlorosilanes has been studied in the greatest detail on *p*-tolyl- and benzyl-trichlorosilanes, and also on phenyl- and *p*-tolyl-methyldichlorosilanes, in the presence of azoisobutyronitrile as initiator.

Chlorination of *p*-tolyl- and benzyl-trichlorosilanes in the presence of this initiator[95,97,285] takes place without cleavage of the reaction products at the silicon–carbon bond. The process can easily be controlled with the formation of compounds of a desired degree of substitution. A distinguishing feature of these reactions is the formation of the monochloro-derivatives in high yields with complete conversion of the initial silane (in contrast to aliphatic chlorosilanes). Among polychloro-derivatives *p*-trichloromethylphenyltrichlorosilane is of practical interest as the starting material for the preparation of *p*-trifluoromethylphenyltrifluorosilane. α*H*-Hexachlorobenzyltrichlorosilane $C_6Cl_5CHClSiCl_3$ has been isolated from the products of the photochemical chlorination of pentachlorobenzyltrichlorosilane[286]; the product of the exhaustive chlorination of benzyltrichlorosilane cannot be obtained.

The chlorination of phenylmethyldichlorosilane can occur selectively—either in the methyl group or in the aromatic ring—depending on the nature of the catalyst. Initiation with azoisobutyronitrile leads to the formation of all possible products in which the methyl group is substituted[287,288]. The ability of the chloromethyl group to be chlorinated more easily than the unsubstituted methyl group is clearly evident in phenylmethyldichlorosilane, just as in the methylchlorosilanes, which is indicated by the ~10% content of the dichloro-derivative in the reaction mixture on conversion of the initial silane. Under otherwise similar conditions the content of polychloro-derivatives in the reaction mixture is appreciably higher in the continuous chlorination of phenylmethyldichlorosilane[289] than with a batch method of chlorination: i.e. the situation is the same as in the chlorination of methylchlorosilanes. The exhaustive chlorination of phenylmethyldichlorosilane in the presence of azoisobutyronitrile at 110–115°C is not accompanied by side-reactions and gives a 90% yield of phenyltrichloromethyldichlorosilane. When the temperature is lowered to 45–50°C, the reaction mixture contains partly chlorinated products; and raising the temperature to 145–150°C lowers appreciably the yield of phenyltrichloromethyldichlorosilane owing to degradation of the chlorination products at the silicon–carbon bond. Because of the high selectivity of the reaction it is desirable to obtain this product by a continuous counterflow scheme[290]. The chlorination of benzylmethyldichlorosilane in the presence of azoisobutyronitrile (at 110°C) results in the formation of αα-dichlorobenzyltrichloromethyldichlorosilane[250]. This compound is obtained also by photochemical chlorination, but then a nuclear addition product, hexachlorocyclohexylmethylmethyldichlorosilane, is also formed[250].

The rate of chlorination of the methyl group in compounds of the type $C_6H_{5-n}Cl_nSiCl_2CH_3$ decreases with increase in *n*.[291] When *n* = 1 the *p*-chloro-isomer is chlorinated considerably more easily than is the *meta*-isomer, although chlorination of *p*-chlorophenylmethyldichlorosilane is slower than that of unsubstituted phenylmethyldichlorosilane.

Sulphuryl chloride proved to be a milder chlorinating agent for phenylmethyldichlorosilane, and was more selective, so that a high yield of phenyldichloromethyldichlorosilane could be obtained[292].

The chlorination of *p*-tolylmethyldichlorosilane in the presence of azoisobutyronitrile at 110–115°C (molar ratio

silane : chlorine = 1 : 3) leads initially to replacement of the nuclear methyl hydrogen atoms. With a large excess of chlorine (1 : 10) *p*-trichloromethylphenyltrichloromethyldichlorosilane is formed in 80% yield[293]. The fact that the aromatic ring of *p*-tolylmethyldichlorosilane contains a substituent of the first kind [*sic*—presumably means +*I* group (Ed. of Translation)] (a methyl group) *para* to the silicon atom weakens the $Si-C_{Ar}$ bond, as is indicated by the greater ease of cleavage of this compound than of phenylmethyldichlorosilane.

2. Addition of Chlorine at Double Bonds and Replacement of Nuclear Hydrogen Atoms by Chlorine

Phenyltrichlorosilane readily undergoes photochemical chlorination at ordinary temperatures (20°C) to form a product—hexachlorocyclohexyltrichlorosilane $C_6H_5Cl_6.SiCl_3$—in which chlorine atoms have added to the aromatic ring[294-296]. The yield decreases with rise in temperature, and at 120°C the photochemical chlorination of phenyltrichlorosilane proceeds solely as a substitution reaction (Fig. 8).

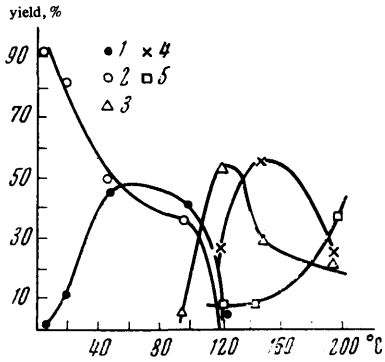


Figure 8. Temperature dependence of yield of products of the photochemical chlorination of phenyltrichlorosilane (for molar ratio $Cl_2 : C_6H_5SiCl_3 = 10 : 1$):
1) $C_6H_5SiCl_3$; 2) $C_6H_5Cl_6SiCl_3$; 3) $C_6H_4ClSiCl_3$; 4) $C_6H_3Cl_2SiCl_3$; 5) $C_6H_2Cl_3SiCl_3$.

The additive chlorination of phenyltrichlorosilane is a chain reaction initiated by free chlorine atoms according to the usual scheme:

$$Cl_2 \xrightarrow{h\nu} Cl^{\cdot} + Cl^{\cdot} \quad (1)$$

$$C_6H_5SiCl_3 + Cl^{\cdot} \rightarrow C_6H_5ClSiCl_3^{\cdot} \quad (2)$$

$$C_6H_5ClSiCl_3^{\cdot} + Cl_2 \rightarrow C_6H_5Cl_2SiCl_3 + Cl^{\cdot}, \text{etc.} \quad (3)$$

A free-radical mechanism is indicated by the fact that additive chlorination can be conducted in the presence of azoisobutyronitrile in the dark[297]. The overall rate of addition is limited by stage (2). Subsequent stages take place at very high rates, so that intermediate addition products—dichlorocyclohexadienyltrichlorosilane and tetrachlorocyclohexenyltrichlorosilane—cannot be detected in the products of the photochlorination of phenyltrichlorosilane: two components—phenyltrichlorosilane and hexachlorocyclohexyltrichlorosilane—are present in the reaction mixture, independently of the molar ratio of the reactants (silane and chlorine) (Fig. 9). The linear dependence of the logarithm of the phenyltrichlorosilane concentration on the duration of chlorination (Fig. 10) indicates that the reaction is of the first order with respect to the silane. The stepwise addition of chlorine to the aromatic ring is proved by the fact that the chain can be terminated by means of iodine, and tetrachlorocyclohexenyltrichlorosilane $C_6H_5Cl_4SiCl_3$ isolated[297].

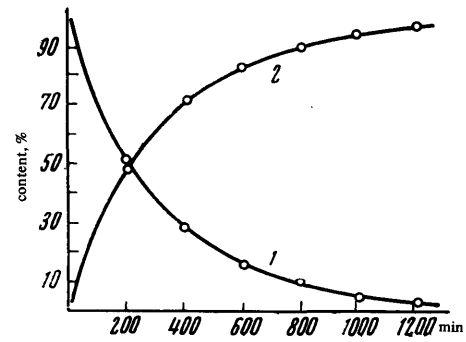


Figure 9. Dependence of composition of reaction mixture on extent of chlorination (at +5°C):
1) $C_6H_5SiCl_3$; 2) $C_6H_5Cl_6SiCl_3$.

The course of the radiation chlorination of phenyltrichlorosilane, initiated by cobalt-60 γ-radiation[18,148], is analogous to the photochemical process.

Hexachlorocyclohexyltrichlorosilane is a mixture of stereoisomers[101]. Its structure is confirmed by the infrared spectrum, which contains no absorption bands characteristic of an aromatic ring. Aqueous alkali hydrolyses this compound with detachment of the hexachlorocyclohexyl radical from the silicon atom. The hexachlorocyclohexane formed as an intermediate is dehydrochlorinated under these conditions and converted into trichlorobenzene. With absolute alcohols hexachlorocyclohexyltrichlorosilane forms the corresponding hexachlorocyclohexylalkoxysilanes. It is inert towards chlorine at 150°C and on exposure to ultraviolet radiation, and also at 75–100°C in the presence of iron(III) chloride. When heated to 550–580°C it splits off hydrogen chloride and is converted into trichlorophenyltrichlorosilane. The product of partial additive chlorination, tetrachlorocyclohexenyltrichlorosilane, is able to eliminate hydrogen chloride at 250°C with the formation of dichlorophenyltrichlorosilane.

Phenyltrifluorosilane forms an addition product, hexachlorocyclohexyltrifluorosilane, more easily than does phenyltrichlorosilane[295].

If the silane contains alkyl radicals as well as the phenyl group, the rate of addition of chlorine to the aromatic ring drops sharply. Thus the photochemical chlorination of phenyltrimethylsilane and *p*-tolyltrichlorosilane involves mainly substitution of the methyl hydrogen atoms, the yield of addition products not exceeding 10–12%.[295] The introduction of halogen atoms and trichloromethyl, trifluoromethyl, and trichlorosilyl groups into the aromatic ring of

phenyltrichlorosilane results in almost complete inhibition of additive chlorination.

Benzyltrichlorosilane gives a high yield of the nuclear addition product hexachlorocyclohexylmethyltrichlorosilane, which is formed on photochemical chlorination together with products in which the methylene hydrogen atoms have been replaced by chlorine[101,285,294].

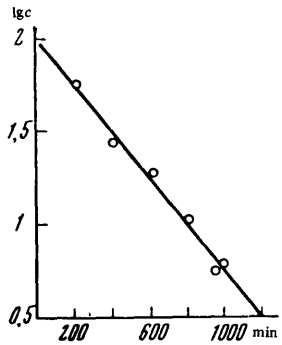


Figure 10. Dependence of logarithm of concentration of phenyltrichlorosilane on duration of chlorination.

Under the same conditions the additive chlorination of diphenyldichlorosilane proceeds relatively easily, but chlorine adds to only one aromatic ring to form hexachlorocyclohexylphenyldichlorosilane $C_6H_5Cl_6SiCl_2C_6H_5$.[295]

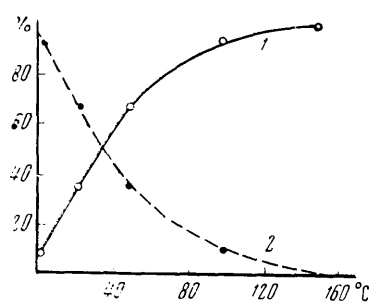


Figure 11. Temperature dependence of composition of products of the photochemical chlorination of phenylmethyldichlorosilane ($Cl_2 : C_6H_5SiCl_2CH_3 = 3.5 : 1$): 1) nuclear addition products; 2) products of substitution in the methyl group.

Addition of chlorine to 1-naphthyltrichlorosilane occurs especially easily with ultraviolet irradiation and a low temperature (0–5°C), but in spite of the prolonged action of excess of chlorine (molar ratio 1-$C_{10}H_7SiCl_3 : Cl_2$ = 1 : 12) the product is 1-$C_{10}H_7Cl_4SiCl_3$.[259,294] This indicates that the addition of chlorine to double bonds probably occurs only in one six-membered ring of 1-naphthyltrichlorosilane. At high temperatures, and also under the influence of iron(III) chloride, the compound 1-$C_{10}H_7Cl_4SiCl_3$ eliminates hydrogen chloride and is converted into dichloro-1-naphthyltrichlorosilane[260].

The action of chlorine on phenylmethyldichlorosilane in daylight at temperatures not above 5°C yields only the nuclear addition product hexachlorocyclohexylmethyldichlorosilane[294,298,299]. Raising the temperature to 20–25°C accelerates substitutive chlorination; at 50°C and above the main product is chlorophenylmethyldichlorosilane. The photochemical chlorination of phenylmethyldichlorosilane at 0°C gives an addition product[299,300]. With rise in temperature substitution in the methyl radical becomes predominant, and is the only process at 95–100°C (Fig. 11). The radical mechanism of formation of hexachlorocyclohexylmethyldichlorosilane is confirmed by the occurrence of additive chlorination in the presence of azoisobutyronitrile at 45–50°C.

The radiation chlorination of phenylmethyldichlorosilane by means of cobalt-60 γ-rays differs from its photochemical chlorination only in that rise in temperature leads to substitution of hydrogen atoms not in the methyl group but chiefly in the aromatic ring[157,169] (Fig. 12). With radiation chlorination the highest yield of chloromethyl products is observed at 20–30°C. Similar results have been obtained for the radiation chlorination of a phenylmethylpolysiloxane polymer[159].

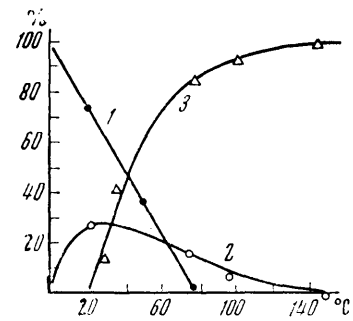


Figure 12. Temperature dependence of composition of products of the radiation chlorination of phenylmethyldichlorosilane: 1) nuclear addition products; 2) products of substitution in the methyl group; 3) nuclear substitution products.

It is interesting that no compounds containing both a hexachlorocyclohexyl radical and di- and tri-chloromethyl groups attached to silicon have been found among the products of the photochemical and radiation chlorination of phenylmethyldichlorosilane. This indicates considerable deactivation of the aromatic ring in phenyltrichloromethyldichlorosilane owing to the presence of the trichloromethyl group. This is confirmed by the exceptional inertness of this compound not only towards thermal and ionic chlorination but also towards additive chlorination[258].

Analysis of the data indicates a definite correlation among the electrophilic character of the substituent, the rate of additive chlorination of substituted aromatic com-

pounds of silicon, and steric hindrance. The sequence of increasing capacity for additive nuclear chlorination in aryl- and alkylaryl-silanes is

$$p\text{-}CF_3C_6H_4SiF_3,\ p\text{-}CCl_3C_6H_4SiCl_3,\ C_6H_4(SiCl_3)_2 < C_6H_4Cl_2SiCl_3 < < C_6H_4ClSiCl_3 < C_6H_5(CCl_3)SiCl_2 < (C_6H_5)_2SiCl_2,$$
$$\alpha\text{-}C_{10}H_7SiCl_3 < C_6H_5SiCl_3 < C_6H_5SiF_3 < C_6H_5(CH_3)SiCl_2,\ C_6H_5CH_2SiCl_3.$$

VII. CHLORINATION OF PHENYLTRICHLOROSILANE IN THE PRESENCE OF IODINE AND ON γ-IRRADIATION

The chlorination of phenyltrichlorosilane is distinguished by interesting features. Depending on the conditions chlorine either adds to the aromatic ring or replaces hydrogen atoms [101]. Photochemical chlorination at 0–50°C involves solely addition of chlorine. With rise in temperature the rate of substitutive chlorination increases with formation mainly of the *o*-chloro-isomer (43%). A similar reaction is observed in the chlorination of phenyltrichlorosilane in the presence of azoisobutyronitrile at 120–125°C. A still stronger shift towards predominant formation of the *o*-chloro-isomer (67%) occurs in the presence of iodine as catalyst [101,241,301]. Thus under the above conditions the trichlorosilyl group loses its inherent *meta*-orienting power.

An interesting property of iodine as catalyst is that it is able to activate equally the nuclear addition of chlorine and its nuclear substitution [101]. Both in the chlorination of benzene in the presence of iodine [302–304] and in that of phenyltrichlorosilane under similar conditions [101] there is simultaneous formation of substitution products (chlorophenyltrichlorosilane) and products of partial additive chlorination (tetrachlorocyclohexenyltrichlorosilane).

The addition of chlorine to an aromatic ring usually takes place by a radical mechanism. Since the formation of atoms and radicals is excluded in chlorination in the presence of iodine, the most probable mode of addition under these conditions must be assumed to be heterolytic, in which the iodine polarises the chlorine and promotes its addition:

$$Cl{-}Cl + I_2 \rightleftarrows \overset{\delta+}{Cl} \ldots \overset{\delta-}{ClI_2}$$

$$C_6H_5SiCl_3 + Cl^+ \rightarrow \left[\text{C}_6\text{H}_5(\text{SiCl}_3)\text{Cl}^+\right] \xrightarrow{+Cl^-} \text{C}_6\text{H}_5(\text{SiCl}_3)\text{Cl}_2 \qquad \text{(I)}$$

$$\text{C}_6\text{H}_5(\text{SiCl}_3)\text{Cl}_2 + Cl^+ \rightarrow \left[\text{C}_6\text{H}_5(\text{SiCl}_3)\text{Cl}_3^+\right] \xrightarrow{+Cl^-} \text{C}_6\text{H}_5(\text{SiCl}_3)\text{Cl}_4 \qquad \text{(II)}$$

The cyclohexadiene system in (I) is highly reactive, and therefore the intermediate dichlorocyclohexadienyltrichlorosilane (I) cannot be isolated from the reaction products. Formation of the dichloro-derivative (I) is confirmed by the appearance among the chlorination products, together with tetrachlorocyclohexenyltrichlorosilane (II), of a considerable quantity of *o*-chlorophenyltrichlorosilane, obviously resulting from dehydrochlorination of (I):

$$\left[\text{C}_6\text{H}_5(\text{SiCl}_3)\text{Cl}_2\right] \xrightarrow{-HCl} \text{C}_6\text{H}_4(\text{SiCl}_3)\text{Cl}$$

This change in the usual electrophilic mechanism of substitutive chlorination probably explains the loss of the *meta*-orienting power of the trichlorosilyl group in the chlorination of phenyltrichlorosilane in the presence of iodine.

The radiation chlorination of phenyltrichlorosilane, initiated by cobalt-60 γ-rays [157] at 0–20°C, involves predominantly nuclear addition of chlorine to form hexachlorocyclohexyltrichlorosilane, and in this respect resembles photochemical chlorination. With rise in temperature nuclear substitution begins, and at 100°C the chlorination of phenyltrichlorosilane already consists solely in substitution. The isomeric composition of the monochlorophenyltrichlorosilane obtained under these conditions shows that in radiation chlorination the chlorosilyl group exerts its normal *meta*-orienting effect (*meta* : *ortho* : *para* = 75 : 20 : 5).

Substitutive chlorination of the phenyl group under the influence of γ-radiation is not inhibited by either oxygen or air. This suggests that the replacement of hydrogen atoms in the aromatic ring of phenyltrichlorosilane during radiation chlorination occurs by an ionic mechanism involving chlorine cations [157,305] formed by the radiolysis of chlorine:

$$Cl_2 \rightsquigarrow \begin{cases} Cl_2^+ + e^- \\ Cl^+ + Cl^- + e^- \end{cases}$$

The radiolysis of silanes is accompanied by the appearance in the reaction mass of excited molecular and splinter ions, which are able to react with a chlorine molecule:

$$[Ion]^+ + Cl_2 \rightarrow [ion]\,Cl + Cl^+$$

The primary Cl^+ ions can then react with a molecule of the initial silane:

$$C_6H_5SiCl_3 + Cl^+ \rightarrow C_6H_4ClSiCl_3 + H^+$$

The proton, on reacting with molecular chlorine, may liberate fresh chlorine ions:

$$H^+ + Cl_2 \rightarrow HCl + Cl^+ + 2.5\ eV$$

Regeneration of Cl^+ ions by these reactions will probably continue until either H^+ or Cl^+ combines with a negative ion, which will correspond to the stage of chain termination.

The only argument against an ionic mechanism for the radiation chlorination of phenyltrichlorosilane is the relatively high temperature of the reaction, since the lifetime of positive ions is too short under these conditions. It increases as the temperature becomes lower, and also in the presence of substances having a high electron affinity and a considerable capture cross-section for thermal electrons. In the present case chlorine and also phenyltrichlorosilane itself may fill this role. Hence there may be factors which promote reaction by an ionic mechanism at high temperatures.

VIII. PREPARATION OF ORGANOSILICON COMPOUNDS CONTAINING FLUORINE (IODINE) IN THE ORGANIC RADICALS

It is not possible to fluorinate organic radicals attached to a silicon atom directly by means of fluorine, because of the accompanying degradation of the molecule to be fluorinated. However, the valuable properties of fluorinated organosilicon polymers have stimulated research aimed at finding other methods for preparation of the corresponding monomers. The principal methods known at present will be described briefly below.

1. Organoelementary Method

The first organosilicon compound containing a fluorine atom in the organic radical was obtained[306] from *p*-fluorophenylmagnesium bromide and trimethylchlorosilane. A large number of diverse compounds of this type have since been obtained by Soviet[307-310] and foreign[311-313] workers. By means of Grignard reagents it is relatively easy to obtain various derivatives from silicon tetrachloride, silicochloroform, tetraethyl orthosilicate, and other compounds. Aromatic and aliphatic fluorine-containing compounds can be used to prepare the Grignard reagent. Compounds based on unsaturated polyfluorides, e.g. tetrakistrifluorovinylsilane[314], can be obtained by the organomagnesium method.

The reactions can be conducted under milder conditions if organolithium compounds are used[315-317], and the yield of the fluorinated organosilicon compounds is higher. In comparison with the use of magnesium that of lithium has not found sufficiently wide application.

Sufficient experimental data have now been published to derive the main principles of the organoelementary synthesis of fluorinated organosilicon compounds.

2. The Swarts Reaction

The Swarts reaction can be used to exchange halogens in an organic radical for fluorine atoms[318]. Halogen atoms attached to silicon are replaced at the same time. To diminish the consumption of antimony trifluoride and antimony pentachloride use is made e.g. of the following scheme[246,319]

$$CH_3C_6H_4SiCl_3 \xrightarrow{HF} CH_3C_6H_4SiF_3 \xrightarrow{+Cl_2} CCl_3C_6H_4SiF_3 \xrightarrow{SbF_3+SbCl_5} CF_3C_6H_4SiF_3$$

Various aryl- and alkyl-fluorosilanes can be obtained by means of the Swarts reaction. Exchange for fluorine depends on the position of the halogen in the organic radical: in 1-bromo-3,3,3-trichlorpropylmethyldichlorosilane and 1,3,3,4,4,4-hexabromobutylphenyldichlorosilane, for example, the 1-bromine atom cannot be replaced by fluorine[320,321].

Several difficulties in conducting the reaction and the limited choice of compounds diminish the possibilities of the Swarts method for introducing fluorine atoms into the organic radicals of alkylsilanes and arylsilanes.

3. Addition at a Silicon–Hydrogen Bond

Many investigations have been undertaken with the aim of obtaining fluorinated organosilanes by the addition of unsaturated fluorine-containing compounds at a silicon–hydrogen bond. This reaction was first accomplished[322,323] in 1954 with the addition of silicochloroform to 1,1-difluoroethylene and tetrafluoroethylene. During many subsequent researches various catalysts and initiators have been found and a large number of diverse compounds have been prepared. Addition is initiated by ultraviolet radiation[324], cobalt-60 γ-rays[325,326], and various compounds such as peroxides[327]. It takes place by a radical–chain mechanism:

$$HSiCl_3 \xleftarrow{h\nu} Cl_3Si^{\cdot} + H^{\cdot} \quad Cl_3Si^{\cdot} + CF_2{=}CF_2 \rightarrow Cl_3SiCF_2CF_2^{\cdot}$$
$$Cl_3SiCF_2CF_2^{\cdot} + HSiCl_3 \rightarrow Cl_3SiCF_2CF_2H + {}^{\cdot}SiCl_3$$

Good results have been obtained by using platinised carbon and especially chloroplatinic acid as catalyst[328,329]. The action of platinum is explained in the literature as involving both heterogeneous and homogeneous catalysis.

Individual examples have been reported of the addition of fluoroalkenes at a silicon–hydrogen bond in the presence of boric acid in an autoclave at high temperatures[330], etc., but they have not interested investigators.

Among all the known methods, addition at a silicon–hydrogen bond is in several cases of the greatest practical interest for the industrial production of fluorinated organosilicon compounds.

4. Other Reactions

In contrast to the well known industrial processes for the direct synthesis of alkyl- and aryl-chlorosilanes, only the simplest halogenated fluorocarbons react directly with a silicon–copper alloy[331], and the yield is low.

Several compounds have been obtained by the Diels–Alder method[332], and by the addition of compounds of the type RCF_2Br or RCF_2I (where R = F or a radical) at the double bonds of alkenylsilanes in the presence of radical initiators[333]. Fluorinated esters[334] and ethers[335] have also been obtained. However, these methods for preparing fluorinated organosilanes have no practical interest.

The literature contains no serious investigations on the preparation of organosilicon compounds containing iodine in the organic radical. Individual publications in which preparations of iodinated organosilanes are encountered are of no theoretical interest and still less of practical interest.

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The Chemical Properties of Thioamides

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The principal chemical properties of thioamides are surveyed—hydrolysis, reduction and oxidation, and reactions with inorganic and organic amines, acid chlorides, aldehydes and ketones, alkyl halides, and halogenated amines, ketones, and acids. A list of 274 references is included.

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I. INTRODUCTION

Thioamides are reactive compounds, and have been well studied. The changes they undergo on oxidation, reduction, reaction with inorganic and organic amines, and addition to halogenated amines, ketones, acids, and esters are widely used in obtaining derivatives of pyrimidine, purine, and uracil, thiazoles, vitamin B_1, etc. [1-16].

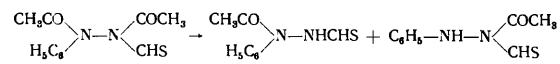
There is a vast literature on the chemical properties of thioamides, which has not yet been systematised. Existing reviews [17-23] are concerned mainly with the preparation of thioamides; the chemical properties are not dealt with adequately [17,18,21-23]. The Soviet literature contains no reviews on the chemical properties of thioamides. This is the reason for publishing the present Review.

II. HYDROLYSIS OF THIOAMIDES

Like amides of carboxylic acids, thioamides can be hydrolysed by water, better in the presence of acids or alkalis. The products are usually carboxylic acids, but sometimes amides and nitriles. Unsubstituted thioamides are relatively easily hydrolysed with the formation in acid medium mainly of carboxylic acids, but in the presence of alkalis aromatic thioamides yield carboxylic acids, nitriles, and amides. Thus thioacetamide is hydrolysed by bases and acids to acetic acid, hydrogen sulphide, and ammonia [24]. With boiling water or hot 1 *N* hydrochloric acid thiobenzamide yields benzoic acid, hydrogen sulphide, and ammonia; but with caustic potash it forms benzonitrile and hydrogen sulphide (ammonia also is formed on heating with 1 *N* caustic potash). [25] Phenylthioacetamide behaves similarly: with dilute hydrochloric acid it gives phenylacetic acid, hydrogen sulphide, and ammonia; but on heating with caustic potash phenylacetonitrile and hydrogen sulphide are obtained [26].

Thioamides are more difficult to hydrolyse than are the corresponding amides [27]. *N*-Thiobenzoylmorpholine is hydrolysed in 10 *N* caustic potash at only one-tenth the rate of *N*-benzoylmorpholine [28].

N-Substituted thioamides are considerably more difficult to hydrolyse than are the unsubstituted compounds. Thus *N*-benzylthiobenzamide hydrolyses very slowly even when boiled in 50% sulphuric acid, whereas thiobenzamide is hydrolysed with the formation of benzoic acid even by boiling water. Phenyl *N*-phenyl-*N*-thiobenzoylthiocarbamate $C_6H_5.CS.N(C_6H_5).CSOC_6H_5$ is hydrolysed slowly by sulphuric acid, one of the products being thiobenzanilide [29]. The hydrolysis of *N*-phenyl-*N'*-thioformyldiacetohydrazide in 10% caustic soda does not affect the thioformyl group, the product being *N'*-phenyl-*N*-thioformylacetohydrazide contaminated with other substances [30]:



The great stability of the thioanilide group in comparison with thiocarbamoyl [31] is evident also in the hydrolysis of *N*-phenyldithio-oxamide: it has proved possible to choose conditions under which only the thiocarbamoyl group is hydrolysed. In the hydrolysis of thioamides of oxalic and oxamic acids the carbon–carbon bond is not broken if a thioanilide group is present, but it is broken in the presence of unsubstituted thiocarbamoyl groups [31].

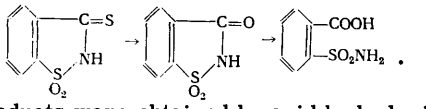
An ester group present in an *N*-substituent can be hydrolysed without decomposition of the thioamide molecule. Thiobenzoylglycine $C_6H_5CS.NH.CH_2.COOH$, which resists the action of alkali in the cold, can be obtained by hydrolysing its ethyl ester with alcoholic caustic potash in the cold [32], but when thiobenzoylglycine is boiled in acid or alkali, sulphur is split off [33], with the formation of hippuric acid, thiobenzoic acid, glycine, and hydrogen sulphide [34].

The hydrolysis of thioamides is substantially influenced also by the nature of the radical attached to the carbon of the thiocarbamoyl group. Thus *N*-β-benzylidynethiopropionylmorpholine $C_6H_5.C\vdots C.CH_2.CS.NC_4H_8O$ is not hydrolysed by boiling for 10 h with 20% alcoholic caustic potash or in concentrated hydrochloric acid; *N*-β-benzylidenethiopropionylmorpholine $C_6H_5.CH:CH.CH_2.CS.NC_4H_8O$, however, is not hydrolysed by alkali under similar conditions, but is hydrolysed by acids [35,36].

Cyclic thioamides are relatively stable to hydrolysis [37].

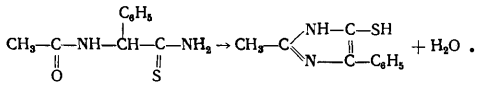
Hydrolysis does not occur when thiosaccharin is treated with sodium carbonate solution in the cold, but the soluble sodium salt of thiosaccharin is formed. The same effect was observed by the action of aqueous ammonia in the cold and on heating, and also with caustic soda solution in the

cold. Boiling with caustic soda hydrolyses thiosaccharin to saccharin, after which cleavage of the ring occurs [38]:



The same products were obtained by acid hydrolysis. Hydrolysis of *o*-sulphamoylthiobenzanilide with hot dilute alkali also gives *o*-sulphamoylbenzoic acid.

Several thioamides undergo cyclisation during alkaline or acid hydrolysis. For example, α-acetamido-α-phenylthioacetamide is rapidly cyclised when heated with a 10% solution of caustic potash [33]:

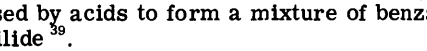


When α-phenyl-α-acetamidothiopropionamide is heated with 20% hydrochloric acid or with dilute caustic potash (with subsequent acidification), it also undergoes cyclisation, to 2,4-dimethyl-4-phenylimidazoline-5-thione [33].

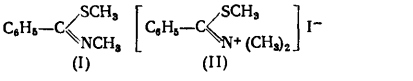
Isothioamides are relatively stable to alkaline hydrolysis, but are easily hydrolysed in the presence of acids†.

Bis-*N*-phenylbenzimidoyl sulphide $C_6H_5.C(:N.C_6H_5).S.C(:N.C_6H_5).C_6H_5$ is stable to hot concentrated alkali, but is easily hydrolysed by acids to form a mixture of benzanilide and thiobenzanilide [39].

Immonium salts of isothioamides are considerably more easily hydrolysed, usually with the formation of good yields of thiolic esters:

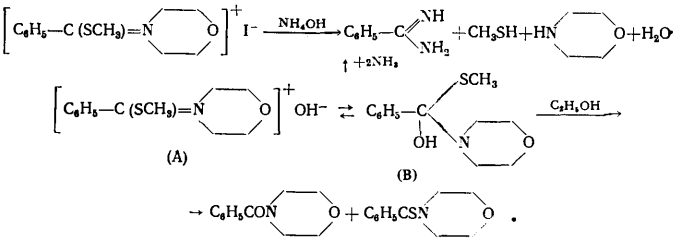


This reaction is used for the hydrolysis of stable thioamides [40]. Thus *N*-phenylthioacetylmorpholine is hydrolysed with difficulty. If, however, it is treated with methyl iodide in acetone, the product‡ is easily hydrolysed by hot water to methyl phenylthioacetate, which is then converted into phenylacetic acid. When ammonia is used instead of hot water, the final product of hydrolysis is phenylthioacetamide.



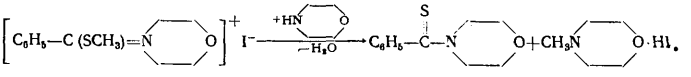
The difference in stability to hydrolysis between isothioamides and their alkylated products—salts of quaternary ammonium bases—can be illustrated by other examples. *S*-Methyl *N*-methylthiobenzimidate (I) is stable in concentrated potassium hydroxide solution, but its quaternary salt (II) is not stable [43]. When (II) is treated with strong alkalis, the methylthio-group is split off and *NN*-dimethylbenzamide is formed. The cation $C_6H_5.C(OH):N(CH_3)_2^+$ is assumed to be formed as an intermediate. A methylthio-group combined with a carbon atom attached to a quaternary nitrogen atom is found to be extremely reactive [42]. Homologues of (I) and (II) behave similarly towards alkaline hydrolysis [42].

The quaternary salt, formed by addition of methyl iodide to *N*-thiobenzoylmorpholine $[C_6H_5.C(S.CH_3):NC_4H_8O]I^-$, dissolves in aqueous ammonia (21°Bé) [44] with the formation of benzamidine. A probable intermediate is the pseudo-base (B) corresponding to the hypothetical hydroxide of the quaternary base (A):

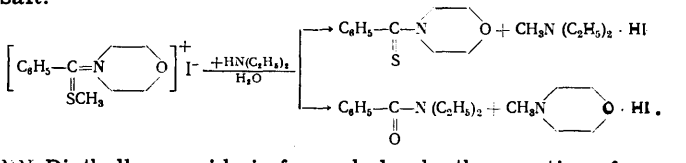


The pseudo-base (B) was isolated [44], but could be not be analysed, although there is other, indirect evidence of its structure. When boiled in alcohol, it is converted into a mixture of *N*-benzoylmorpholine and *N*-thiobenzoylmorpholine with the liberation of methanethiol or methanol. A quaternary salt was obtained with hydrogen iodide. On treatment with aqueous ammonia the pseudo-base (B) gives benzamidine [44].

The quaternary salt reacts similarly with primary amines [44]. *NN'*-Dimethylbenzamidine has been obtained by the action of methylamine. However, hydrolysis with an aqueous solution of a secondary amine follows a different path, the quaternary salt now acting as a methylating agent. Reaction with morpholine gave *N*-thiobenzoylmorpholine and *N*-methylmorpholine:



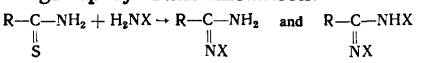
With diethylamine the main product *N*-thiobenzoylmorpholine was accompanied by a small quantity of *NN*-diethylbenzamide, the normal hydrolysis product of the quaternary salt:



NN-Diethylbenzamide is formed also by the reaction of ethyl thiobenzoate with diethylamine. In the presence of tertiary amines hydrolysis of the salt yields only thiolic esters [44]. Other examples are known of the hydrolysis of unsubstituted and substituted thioamides and isothioamides [45-47].

III. REACTIONS OF THIOAMIDES WITH INORGANIC AND ORGANIC AMINES AND SODIUM AZIDE

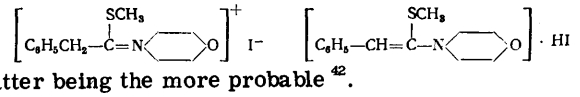
The reaction of thioamides with inorganic amines (hydroxylamine and hydrazine) is accompanied by replacement of sulphur by the amine residue and sometimes by the amino-group by transamidation:



where X = OH, NH_2, NHR^1, NR^1R^2.

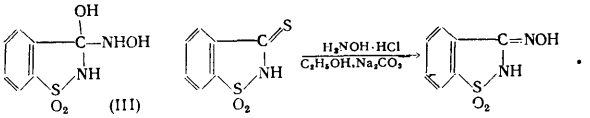
†Isothioamides, being strong bases, give salts with strong mineral acids, but excess of acid hydrolyses them to thiolic esters and ammonium chloride. In this respect the dibenzoyl derivative of thiobenzoxamic acid $C_6H_5.C(S.CO.C_6H_5):N.CO.CO.C_6H_5$ is exceptional: it is stable to hydrolysis in boiling dilute hydrochloric acid, but is hydrolysed by alcoholic caustic potash. The hydrolysis products are benzoxamic and thiobenzoic acids contaminated by thiobenzoxamic and benzoic acids [41].

‡Two structures are possible for the addition product of methyl iodide and *N*-phenylthioacetylmorpholine



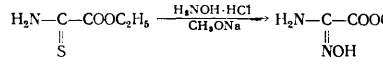
the latter being the more probable [42].

Thiobenzamide when boiled with an alcoholic solution of hydroxylamine gives hydroxyiminobenzamide [48,49]. When *NN'*-diphenyldithio-oxamide $C_6H_5.NH.CS.CS.NH.C_6H_5$ is treated with hydroxylamine, dihydroxyimino-*NN'*-dithio-oxamide $C_6H_5.NH.C(:N.OH).C(:N.OH).NH.C_6H_5$ is formed [49]. Rubeanic acid reacts with hydroxylamine hydrochloride in alcoholic sodium carbonate solution for form dihydroxy-imino-oxamide [50]. Under the same conditions saccharin yields the stable addition product (III), and thiosaccharin yields a hydroxyiminoamide [51]:

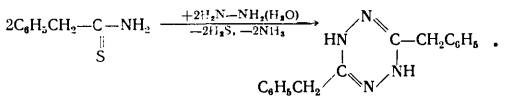


It is assumed that an addition product is formed initially with thiosaccharin also, from which hydrogen sulphide splits off [51].

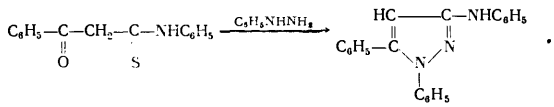
Ethyl thio-oxamate reacts with hydroxylamine hydrochloride in alcoholic sodium methoxide solution to give ethyl hydroxyimino-oxamate [52]:



The reaction between thioamides and aqueous solutions of hydrazine involves replacement of sulphur and trans-amidation with the formation of 3,6-disubstituted 1,4-di-hydro-1,2,4,5-tetrazines [53]:

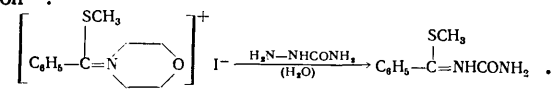


β-Carbonylthioamides (or addition products of enamines and isothiocyanates) react with hydrazine or phenyl-hydrazine to form aminopyrazoles [54]:

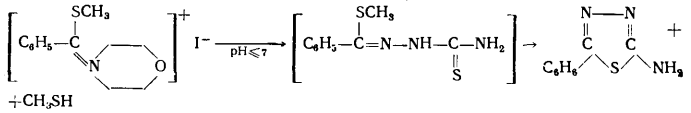


3-Anilino-1,5-diphenylpyrazole

3-Anilino-4-ethylpyrazole and 3-anilino-5-phenylpyrazole have been obtained in this way (by boiling the corresponding thioamides with ethanolic hydrazine for $1\frac{1}{2}$–2 h). Hydrazine reacts similarly with other thioamides [55]. With mono- and di-thio-oxamides sulphur is replaced by the hydrazine residue [56–58]. The isothioamide, *N*-*α*-methylthiobenzyli-denemorpholinium iodide $[C_6H_5.C(S.CH_3):NC_4H_8O]^+I^-$, reacts with excess of hydrazine to give a good yield of 1,4-dihydro-3,6-diphenyl-1,2,4,5-tetrazine [44]. The same compound is formed by the action of hydrazine on thio-benzamide [53]. The above morpholinium iodide does not give a cyclic product with semicarbazide in aqueous solution [59]:



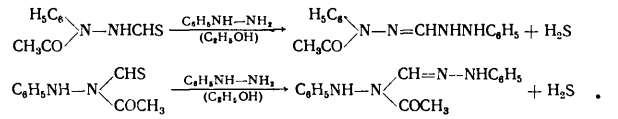
But cyclisation occurs with thiosemicarbazide in acid or neutral medium to form 2-amino 5-phenyl-1,3,4-thiadia-zole. It is supposed that even here the primary product is analogous to that obtained with semicarbazide, but methanethiol is then eliminated to give the thiadiazole [60]:



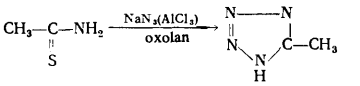
+CH_3SH

If these reagents interact in the presence of weak or strong bases in aqueous solution or in non-aqueous solvents, cyclisation does not occur, but 1-*α*-morpholino-benzylidenethiosemicarbazide is formed. In dilute acids this compound is cyclised to 1,3,4-thiadiazole [60].

The reaction of acylated phenylthioformylhydrazides with phenylhydrazine involves replacement of sulphur by the phenylhydrazine residue:



With sodium azide thioamides form tetrazoles. Thio-acetamide reacts with excess of sodium azide in the presence of aluminium chloride in oxolan to give 5-methyl-tetrazole (yield 55%):[61]



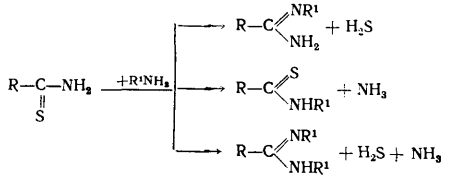
Similarly pentamethylenetetrazole (Cardiazole) has been obtained from *ε*-caprolactam. Since nitriles also give tetrazoles with sodium azide, it is assumed that nitriles are formed as intermediates in these reactions.

Thioamides and isothioamides react differently with primary, secondary, and tertiary amines.

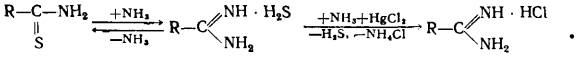
Tertiary amines, being acceptors of hydrogen sulphide, decompose thioamides to the nitrile and hydrogen sulphide. Boiling thioacetamide or thiobenzamide in pyridine yields the corresponding nitrile and hydrogen sulphide [62]. Pyri-dine initiates this reaction by forming the pyridinium salt of the thioamide.

Secondary amines usually transamidate thioamides: in ethereal solution thioacetamide and piperidine yield *N*-thioacetylpiperidine [63]; and diethylamine and thioform-amide give *NN*-diethylthioformamide [94].

Primary amines, like inorganic amines, replace the sulphur by the amine residue and effect transamidation with the formation of *N*-substituted amidines, *N*-substituted thioamides, or mixtures of these products:

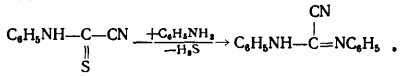


The formation of salts of amidines by the reaction of aliphatic and aromatic thioamides with concentrated solu-tions of ammonium hydroxide was established as long ago as the nineteenth century [65,66]. The yield of amidines was increased by adding mercury(II) chloride, which shifted the equilibrium by forming mercury sulphide:



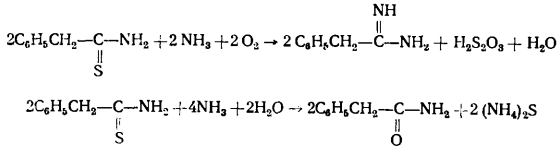
The action of primary amines under similar conditions yields *N*-substituted amidines. Aniline hydrochloride reacts with phenylthioacetamide in absolute ethanol to form *N*-phenylacetamidine [67], and with thiobenzamide to give *N*-phenyl- and *NN'*-diphenyl-benzamidines [68]. *NN'*-Diphen-ylbenzamidine has been obtained by the reaction of thio-benzanilide with molten aniline hydrochloride [69].

The reaction of thio-oxanilonitrile with aniline in boiling benzene gives the amidine in 40% yield, the nitrile group being unaffected [70]:



With change in the conditions the amidine undergoes hydrolysis with formation of the corresponding amide.

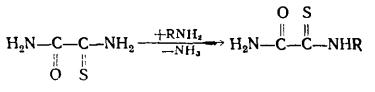
Phenylthioacetamide reacts with ammonium hydroxide solution at room temperature to form phenylacetamidine and a thiosulphate:



and on boiling to give phenylacetamide and ammonium sulphide [95].

With *NN'*-disubstituted thioamides (e.g. dimethylthioformamide) primary amines form *NNN'*-trisubstituted amidines. Thus *NN'*-dimethyl-*N*-naphth-1-ylformamidine has been isolated as its complex with trinitrobenzene by boiling a mixture of dimethylthioformamide, 1-naphthylamine, and sodium methoxide [71].

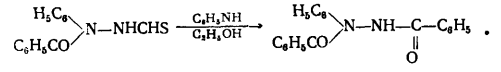
Thioamides undergo transamidation on being heated with amines. Ammonia is evolved when thioacetamide is boiled in butylamine, with the formation of *N*-butylthioacetamide, the yield being almost theoretical [70]. This reaction has been used to obtain several *N*-alkyl- and *N*-aryl-thioamides and *NN'*-dialkyl- and *NN'*-diaralkyldithio-oxamides [70,72-74]. It should be noted that only the thiocarbamoyl group is involved in this reaction, the carbamoyl group being unaffected. The interaction of monothio-oxamide with various amines yields *N*-alkylmonothio-oxamides [75]:



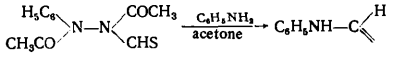
where R = CH_3, C_4H_9, $C_{12}H_{25}$.

A mixture of a thioamide and an amine can be replaced by a mixture of the amide, phosphorus pentasulphide, and the amine: the thioamide obtained initially reacts with the amine to form *N*-substituted derivatives. Aliphatic, aromatic, aliphatic–aromatic, and heterocyclic amines and diamines have been used in this reaction [64,76].

N-Benzoyl-*N*-phenyl-*N'*-thioformylhydrazide reacts differently with aniline when boiled in aqueous–alcoholic solution [77]:

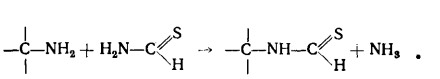


Diacetylphenylthioformylhydrazide reacts with aniline in acetone as follows [30]:

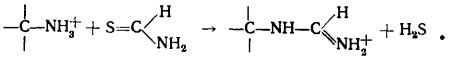


The reaction between thioamides and amines has been studied also in the case of thioformamide and amino-acids [63]. The carbonates of arginine and L-lysine, and also the ethyl ester of glycine, react with thioformamide in methanol at room temperature to give crystalline products. Glycine, L-leucine, DL-alanine, and histidine with excess of thioformamide yield similar products only on being heated to 60°C.

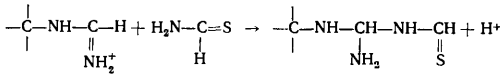
Only amino-acids containing free amino-groups react easily with thioformamide, the products being thioformyl derivatives:



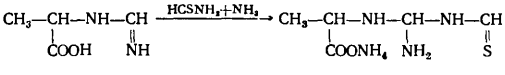
The amino-groups of monoamino-acids (glycine, DL-alanine, L-leucine), the terminal amino-group of L-lysine, and the NH group in the imidazole ring of histidine, which are present as amphoteric ammonium ions, react with thioformamide at 60°C with the elimination of hydrogen sulphide and the formation of formamidine derivatives:



In the cases of L-leucine, DL-alanine, and L-lysine the latter react with a second thioformamide molecule:



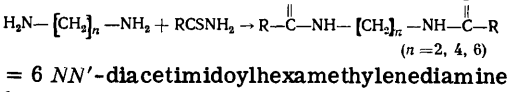
N-Formimidoyl-alanine and -leucine react with molten thioformamide and with ammonia to give products identical with those obtained from the amino-acids and thioformamide at 60°C:[78]



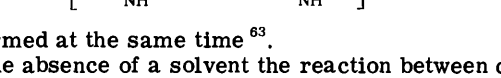
Thioformamide reacts in the cold also with proteins. The products, "thioproteins", are probably analogous to those obtained with amino-acids [63,79,80].

Sometimes thioamides do not react with ammonia and primary amines. For example, the ester group in ethyl monothio-oxamate $N_2N.CS.COOC_2H_5$ is probably converted into a carbamoyl group, while the thiocarbamoyl group plays no part in the reaction [81]. Alcoholic solutions of ammonia or the primary amine have been used. Treatment of ethyl thio-oxamate or ethyl thio-oxanilate $C_6H_5.NH.CS.COOC_2H_5$ with aniline at 140°C gives monothio-oxanilide $C_6H_5.NH.CS.CO.NH.C_6H_5$. [82,83]

Diamines (ethylene-, tetramethylene, hexamethylene-) react with monothioamides in ethereal solution to form *NN'*-dithioacyl derivatives [63]:

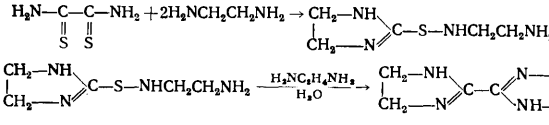


When *n* = 6 *NN'*-diacetimidoylhexamethylenediamine thiosulphate

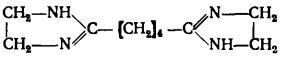


was formed at the same time [63].

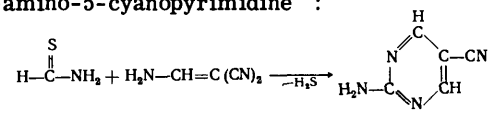
In the absence of a solvent the reaction between dithio-oxamide and ethylenediamine hydrate involves transamidation and replacement of sulphur by an imido-group to give 2,2'-bi-imidazolinyl [84]. In hot alcoholic solution (molar ratio of dithio-oxamide to diamine = 1 : 2) 2-2'-aminoethylaminothio-Δ^2-imidazoline was isolated as an intermediate product. [85] On being heated with ethylenediamine hydrate this compound is converted into 2,2'-bi-imidazolinyl:



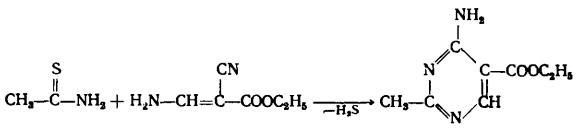
Ethylenediamine hydrate reacts with dithioadipamide, both in the absence of solvent and in alcohol, also with the formation of a cyclic product—tetramethylene-2,2′-bis-imidazoline



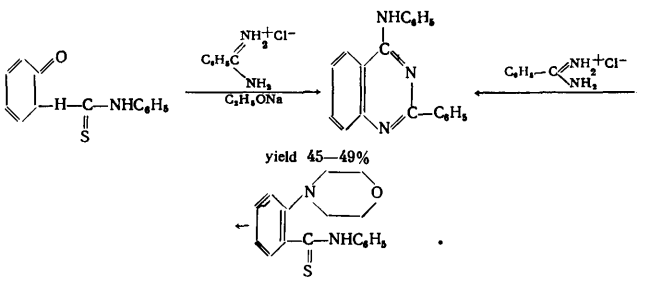
The reactions between thioamides and amines are widely used for synthesising pyrimidine and purine derivatives. Thioformamide reacts with aminomethylene-malononitrile on boiling with alcoholic sodium ethoxide to form 2-amino-5-cyanopyrimidine [86]:



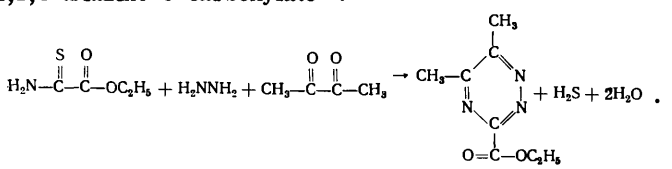
Under similar conditions thioacetamide reacts with ethyl β-amino-α-cyanoacrylate $H_2N.CH:C(CN).COOC_2H_5$ to give ethyl 4-amino-2-methylpyrimidine-5-carboxylate [87]:



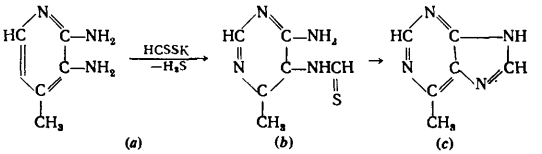
Pyrimidine derivatives are obtained also by the reaction of β-carbonylthioamides with benzamidine in the presence of sodium ethoxide [54]:



The action of ethyl monothio-oxamate on hydrazine and butane-2,3-dione gives a good yield of ethyl 5,6-dimethyl-1,2,4-triazine-3-carboxylate [88]:

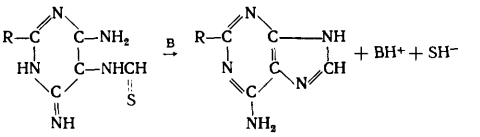


The reaction of 4,5-diamino-6-methylpyrimidine (*a*) with a salt of dithioformic acid gives 4-amino-6-methyl-5-thioformamidopyrimidine (*b*), which cyclises into a purine derivative (*c*) by interaction of the amino- and thioamido-groups:



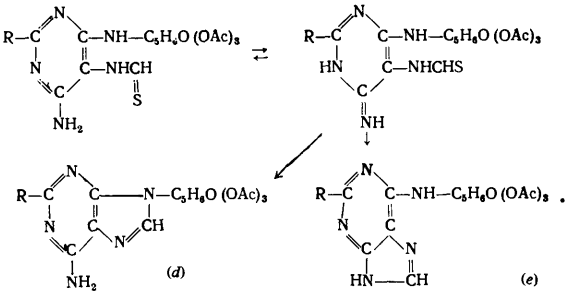
The reaction is conducted in hot pyridine or quinoline solution or in a solution of sodium ethoxide in anhydrous alcohol. In aqueous solution the yield is often diminished by hydrolysis of the thioformamide. The best media for this reaction are alcoholic solutions of sodium ethoxide, although the reaction is then slower than in excess of pyridine or quinoline, but the yields are considerably higher. The molar ratio of the pyrimidine derivative to the alkoxide is 1 : 1. [89]

Pyrimidine derivatives containing a 2-methylthio-group (e.g. 4,6-diamino-2-methylthio-5-thioformamido-pyrimidine) are the easiest to cyclise [89]. It is assumed that ring closure is effected by the action of the base on a tautomeric form of the pyrimidine [83,89]:

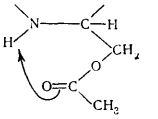


where R = H, CH_3, CH_3S.

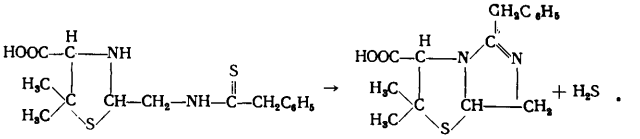
The cyclisation of 4-amino-6-glucosidoamino-5-thio-formamidopyrimidine, its triacetyl derivative, and many other compounds has also been accomplished [89]:



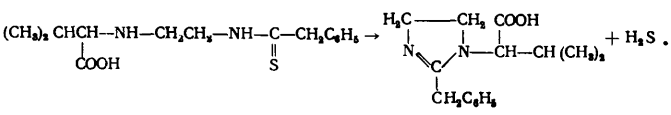
Cyclisation in alcoholic sodium ethoxide yielded in all cases only the 9-glucosidoaminopurines (*d*): the isomeric 6-glucosidoaminopurines (*e*) were not formed. Since the 6-triacetylglucosidoaminopyrimidine is easily deacetylated, it is cyclised in pyridine or in a solution of potassium acetate and acetic acid in anhydrous acetonitrile. In these cases not only the 9-triacetylglucosidoaminopurine but also a considerable yield of the 6-triacetylglucosido-aminopurine (*e*) are formed [90]. Cyclisation is assumed to involve formation of an intermediate product by hydrogen bonding between the 2′-acetyl group of the sugar residue and the hydrogen of the glucosidic NH group. Such ring closure induces a negative charge on the glucosidic nitrogen and thereby enhances the reactivity of the 6-amino-group:



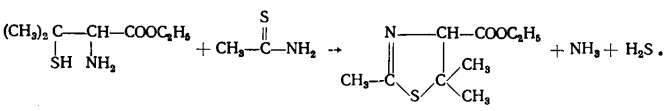
Heterocyclic systems other than purine derivatives have been obtained in a similar manner. Thus boiling 5,5-dimethyl-2-phenylthioacetamidomethylthiazolidine-4-carboxylic acid in quinoline yields benzylpenillamine [91,92]:



The ethyl ester of this acid could not be made to react [93]. The next example of the preparation of heterocycles is the synthesis of imidazoline derivatives [94]:



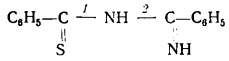
The ethyl ester of penicillamine with thioacetamide forms ethyl 2,5,5-trimethyl-Δ^2-thiazoline-4-carboxylate [95]:



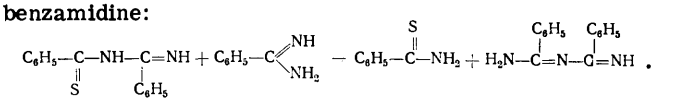
Investigation of the reactions of *N*-benzimidoylthiobenzamide $C_6H_5.CS.N:C(NH_2).C_6H_5$ with ammonia, amines, and amidines [81] indicated that this thioamide is stable in an alcoholic solution of aniline for several days. On addition of mercuric oxide, however, *N'*-*N''*-phenylbenzimidoylbenzamidine $C_6H_5.N:C(C_6H_5).N:C(C_6H_5).NH_2$ was formed rapidly [96]. In alcoholic ammonia and in the absence of a desulphurising agent, *N*-benzimidoylthiobenzamide is rapidly split into benzamidine, thiobenzamide, triphenyltriazine, 3,5-diphenyl-1,2,4-thiadiazole, and nitrogen- and sulphur-containing compounds of basic character, whose structure has not been established [96]. The disubstituted 1,2,4-thiadiazole is probably formed by oxidation of thiobenzamide [97] and *N*-benzimidoylthiobenzamide [98].

The reaction between *N*-benzimidoylthiobenzamide and benzylamine at room temperature gave thiobenzamide (58.5%), *N*-benzylbenzamidine (78%, as the picrate), *N*-benzylthiobenzamide (3.5%), and benzamidine (1.2%, as the picrate). *N*-Benzylbenzamidine and *N*-benzylthiobenzamide were probably formed by secondary reactions of benzylamine with benzamidine and thiobenzamide respectively.

It is assumed that *N*-benzimidoylthiobenzamide

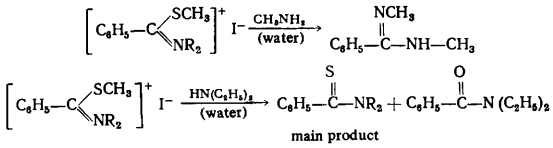


is cleaved both by ammonia and by benzylamine mainly at bond *2*. This occurs also with benzamidine, when the main products are thiobenzamide and *N'*-benzimidoylbenzamidine:

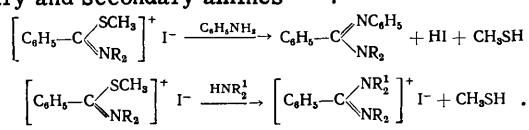


In contrast to benzamidine, substituted amidines—*N*-phenylbenzamidine and *N*-benzylbenzamidine—do not react with *N*-benzimidoylthiobenzamide at room temperature. In boiling benzene, however, *N*-phenylbenzamidine forms small amounts of triphenyltriazine and *N*-phenyl-*N'*-*N''*-phenylbenzimidoylbenzamidine $C_6H_5.N:C(C_6H_5).N:C(C_6H_5).NH.C_6H_5$. The latter product results either from disproportionation of the triphenyldiamine or from a secondary reaction with benzamidine.

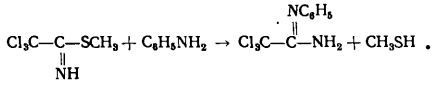
S- and *N*-Substituted thioamides and their salts react with primary, secondary, and tertiary amines in aqueous solution as follows [60]:



In non-aqueous media these salts react differently with primary and secondary amines [40,48]:



The action of alkylthioamides on aniline is a general method for obtaining *N*-phenylamidines [46,99,100]:



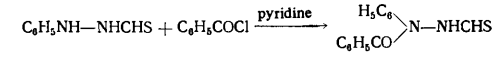
The thermal stability of alkyl thioimidate hydrochlorides increases as the alkyl group becomes larger.

IV. REACTIONS OF THIOAMIDES WITH ACID CHLORIDES

The reactions of thioamides with chlorides of carboxylic acids, imidoyl chlorides, sulphur monochloride and dichloride, thionyl chloride, sulphuryl chloride, and benzenesulphonyl chloride have been studied. With chlorides of carboxylic acids the main reaction is acylation of the thioamides, *N*-substituted thioamides are formed with imidoyl chlorides, and with the other reagents *N*-imidoylthioamides and their oxidation products are formed.

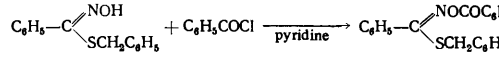
Thioacetamide reacts with acetyl chloride to give an extremely unstable crystalline product [101].

A few cases of benzoylation have been reported. The action of benzoyl chloride on a warm solution of thiocamphorimide, ethyl iodide, and magnesium produces benzoylation of the imido-group of thiocamphorimide [102]. The acylation of 2-phenyl-1-thioformylhydrazide by benzoyl chloride in pyridine leads to the formation of 2-benzoyl-2-phenyl-1-thioformylhydrazide:



the product being soluble in alkalis. If two equivalents of benzoyl chloride are used, the product is insoluble in alkalis. A similar reaction occurs with acetyl chloride.

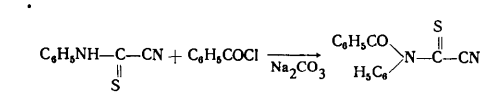
Benzoyl chloride reacts also with *S*-benzyl thiobenzohydroximate in pyridine [41]:



Salts of *N*-benzylthioacetamide and *N*-benzylthiobenzamide are easily acylated by acetyl and benzoyl chlorides [103]:

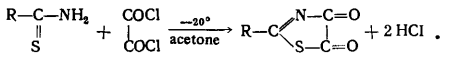
where $R^1 = CH_3$, C_6H_5.

The benzoylation of thio-oxanilonitrile in aqueous sodium carbonate solution yields benzoylthio-oxanilonitrile [104]:



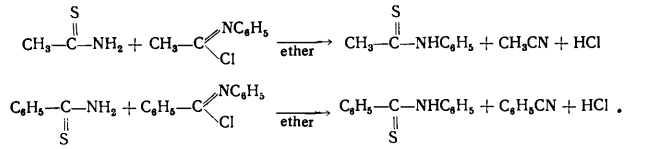
but in caustic soda solution the amide $C_6H_5.CO.N(C_6H_5).CS.CO.NH_2$ is obtained.

The action of thioamides on oxalyl chloride (either in the absence of a base or in the presence of e.g. pyridine) produces derivatives of thiazoline-4,5-dione [105]:

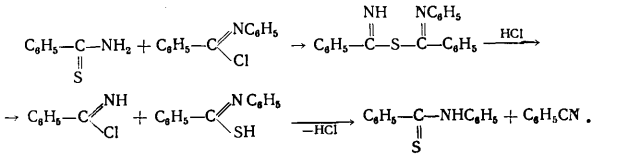


With cyclohexylthioamide in the absence of a base the acid-catalysed elimination of cyclohexene takes place [105].

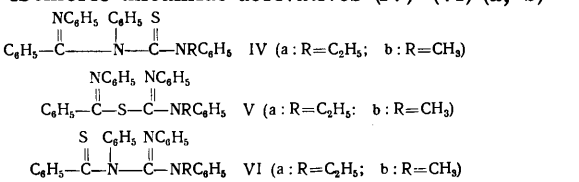
Unsubstituted thiobenzamide and thioacetamide react with *N*-phenylimidoyl chlorides in ethereal solution to form thioanilides [106]:



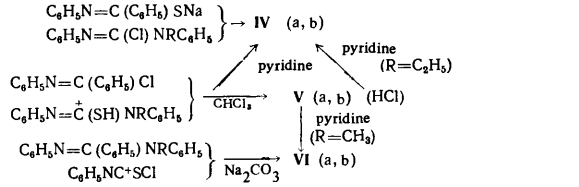
This reaction, like that of nitriles with thioamides, involves the intermediate formation of a product which is cleaved by hydrogen chloride into thiobenzanilide and benzonitrile:



Three isomeric thioamide derivatives (IV)–(VI) (a, b)

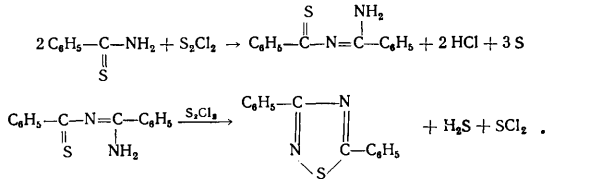


have been obtained by the reaction of thioamides with an imidoyl chloride [107] (scheme cited in Ref. 18):



Reaction of the sodium salt of thiobenzanilide with the imidoyl chloride $C_6H_5.N:CCl.NR.C_6H_5$ ($R = C_2H_5$, CH_3) did not yield the expected product (V), but (IV) was formed. Treatment of the hydrochlorides of (Va) and (Vb) with pyridine results in (IVa) and (VIb) respectively, the main product being the free base (V) in both cases. When (VIa) is heated it is converted into (IVa), and (IVb) into (VIb). In these cases also (V) is an intermediate product.

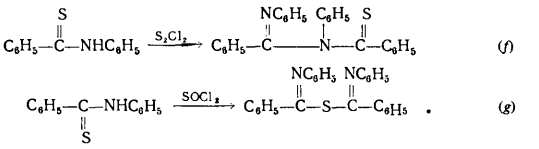
On the slow addition of sulphur monochloride to a solution of thiobenzamide in ether in the cold [104,108] *N*-benzimidoylthiobenzamide and 3,5-diphenyl-1,2,4-thiadiazole are formed, the latter being an oxidation product of the former [109]:



N-Benzimidoylthiobenzamide separates also when the reaction is conducted in alcoholic potassium carbonate solution. The same products are obtained by the interaction of thiobenzamide and thionyl chloride in ether in the cold, when sulphur, sulphur dioxide, and hydrogen chloride are also liberated [39]. Thiobenzamide and other thioamides react similarly with sulphuryl and benzenesulphonyl chlorides: in the latter case the main products are 3,5-diphenyl-1,2,4-thiadiazole and sulphur [39], and in the former case *N*-benzimidoylthiobenzamide.

On reaction of thioacetamide with thionyl chloride, thioacetamide, sulphur, sulphur dioxide, and hydrogen chloride separate. The same result is obtained by the action of thionyl chloride on thioacetanilide.

Sulphur monochloride and thionyl chloride give different products with the same thioamide. With thiobenzanilide the former yields *N*-*N'*-phenylbenzimidoylthiobenzanilide (*f*) and the latter the isomeric product di-*N*-phenylbenzimidoyl sulphide (*g*):[39]



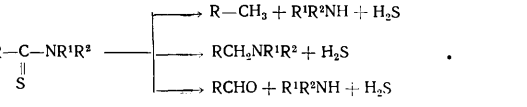
However, the structures of products (*f*) and (*g*) have not been proved. In both cases sulphur, aniline hydrochloride, and benzanilide were isolated§.

Thiobenzanilide forms with benzenesulphonyl chloride a small quantity of *N*-*N'*-phenylbenzimidoylthiobenzanilide, the yield of which is increased by using the sodium salt of thiobenzanilide. Another product of the reaction is benzenethiosulphonic acid $C_6H_5.SO_2SH$. [39]

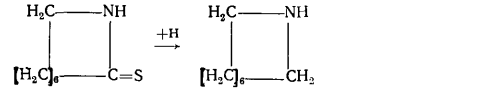
Substituted thioformamides $HCS.NR_2$ react with sulphur monochloride, sulphur dichloride, and thionyl chloride in the presence of pyridine in dichloromethane to form the chlorothioformamides $ClCS.NR_2$ (i.e. they are chlorinated. [111]

V. REDUCTION OF THIOAMIDES

Thioamides are reduced in the presence of Raney nickel in neutral solvents, by the action of metals in acid medium and of metal amalgams, and electrolytically [112,113]. Depending on the method of reduction the products are hydrocarbons, amines, aldehydes, and other substances:



The methods of reduction differ substantially in their effectiveness. For example, the lactam of the thioamide of ω-amino-octanoic acid (perhydroazonine-2-thione) is not reduced by magnesium amalgam in moist ether, by aluminium amalgam in aqueous alcohol, or by zinc dust in acetic acid [38], whereas sodium in glacial acetic acid yields a small quantity of perhydroazonine, and electrolytic reduction in 55% sulphuric acid with a lead cathode at 30°C gives an 85% yield of perhydroazonine [38]:



We shall examine below all the above methods for reducing thioamides.

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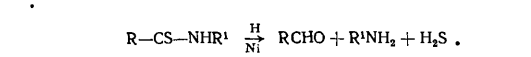
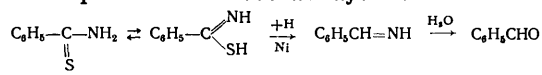
§Benzanilide is probably formed by decomposition of the sulphide $C_6H_5.N:C(C_6H_5).S.C(C_6H_5):N.C_6H_5$ (or its isomer). If this sulphide is treated initially with hydrogen chloride in absolute ether, and then with dilute sodium hydroxide solution, it is split into benzanilide and thiobenzanilide [110].

1. Reduction of Thioamides in the Presence of Raney Nickel [114]

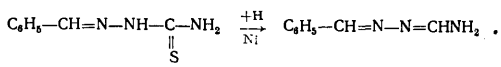
The course of the reduction of thioamides may vary with the nature of the Raney nickel. In the presence of Raney nickel which has been partly deactivated in boiling acetone the thioamide is reduced to the aldehyde in good yield [115]:



Thus the corresponding aldehydes were obtained when thiobenzamide and thio-*p*-toluamide were reduced in ethanol at room temperature for several days [116]:

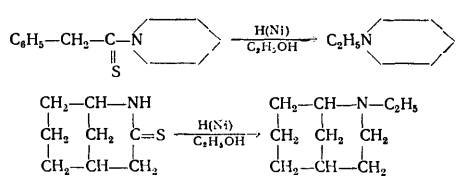


Desulphurisation of the thioamide and formation of a carbon–nitrogen bond are observed also in other cases. Thiourea and its derivatives are reduced to formamidines [117,118]. Thiosemicarbazones are reduced similarly [119]:

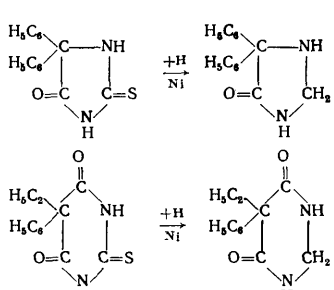


Reduction on Raney nickel prepared in the usual way converts thiocarbonyl into methylene groups [120].

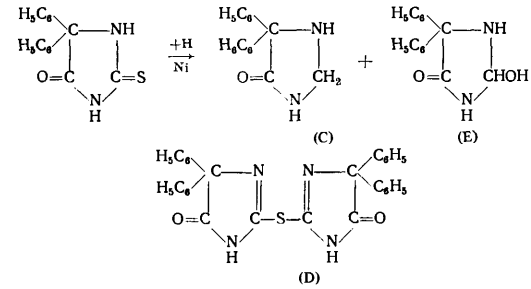
The solvent has a substantial influence on the reduction. With *N*-phenylthioacetylmorpholine in 8% alcohol ethylmorpholine and ethylbenzene are formed in quantitative yield as a result of *N*-ethylation, but in dioxan phenethylmorpholine is obtained [120]. *N*-Ethylation occurs on reduction in ethanol in other cases. For example, the thiopiperidide of phenylacetic acid gives a 44% yield of *N*-ethylpiperidine [120,121], and the thiolactam of 3′-aminocyclohexylacetic acid a 76% yield of 2-ethyl-2-azabicyclo-[3,3,1]nonane [122]:



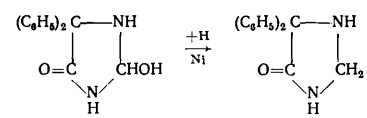
The reduction of heterocyclic thioamides has been studied in detail on thiohydantoins and thiobarbituric acids. The reduction of these compounds in ethanolic solution (boiling for 2–5 h) leads to replacement of sulphur by hydrogen and formation of the normal reduction products. Examples are the reduction of 5,5-diphenyl-2-thiohydantoin [123,124], and of 5-ethyl-5-phenyl-2-thiobarbituric acid [125–128]:



When the thiohydantoin is reduced under milder conditions (ratio of thiohydantoin to Raney nickel 1 : 5 by weight, boiled for 30 min), approximately equal quantities of 4-oxo-5,5-diphenylimidazolidine (C) and bis-5-oxo-4,4-diphenyl-Δ^2-imidazolin-2-yl sulphide (D) are formed together with a small quantity of 2-hydroxy-4-oxo-5,5-diphenylimidazolidine (E):[129]

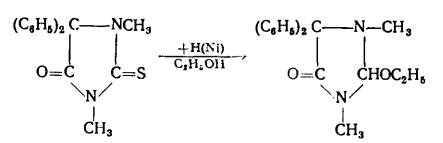


Further reduction in the presence of Raney nickel in boiling ethanol for 2 h converts (E) into a good yield of the imidazolidone [129]:



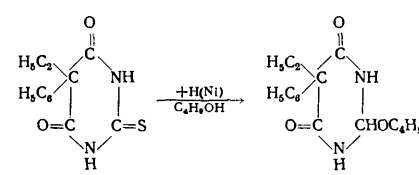
2-Hydroxy-derivatives analogous to (E) are formed also by the reduction of other thiohydantoin derivatives [123].

Tetra-substituted thiohydantoins on reduction in ethanolic solution are ethoxylated (cf. *N*-alkylation) with the formation of 2-ethoxy-derivatives [129]:



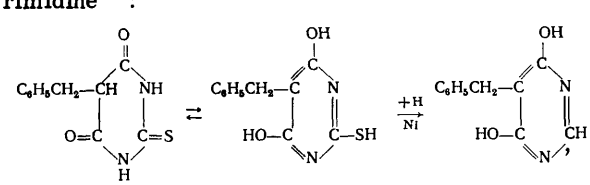
Replacement of ethanol by methanol, propan-1-ol, and cyclohexanol yields the corresponding 4-oxoimidazolidines [129].

The reduction of derivatives of thiobarbituric acid yields initially the 2-alkoxy-derivatives [129]:



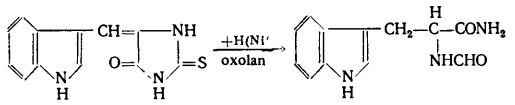
On further treatment with hydrogen both alkoxy- and hydroxy-derivatives are converted with quantitative yields into the normal reduction products [129].

5-Mono-substituted 2-thiobarbituric acids react on reduction in the tautomeric pyrimidine-2-thiol form, since the product of the reaction is always a 4,6-dihydroxypyrimidine [129]:

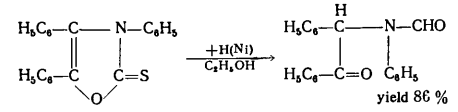


When 5-alkylidene- and 5-benzylidene-2-thiohydantoins are reduced in moist oxolan solution, the thiohydantoin

ring undergoes fission with the formation of amides of α-formylamino-acids:



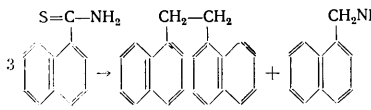
This reaction is used for the preparation of α-amino-acids [124]. 3,4,5-Triphenyl-Δ^3-oxazoline-2-thione in ethanol undergoes analogous reduction [130]:



Other examples of reduction with Raney nickel will be found in Refs. 131–142.

2. Reduction of Thioamides by Metals in Acid Medium and by Metal Hydrides

The reduction of thioamides by this method often yields hydrocarbons, amines [143], and aldehydes. 1,2-Di-1'-naphthylethane and 1-naphthylmethylamine have been obtained on reduction of the thioamide of 1-naphthoic acid:



Thiobenzamide on reduction gives stilbene, benzylamine, and 1,2-diphenylethane. The action of zinc and hydrochloric acid on *N*-benzimidoylthiobenzamide $C_6H_5.CS.NH.C(:NH).C_6H_5$ gives only *N*-benzylbenzamidine $C_6H_5.CH_2.NH.C(C_6H_5):NH$, [144] and *m*-ethoxythiobenzamide gives *m*-ethoxybenzylamine [145]. When iron powder is heated with thiobenzamide in 50% acid for 4 days a 60% yield of benzaldehyde is obtained [146]¶. Tin in hydrochloric acid converts *N*-benzyl-*p*-nitrothiobenzamide into *N*-benzyl-*p*-aminothiobenzamide (yield 95%): the thiocarbamoyl group is not reduced [148].

Reduction of thiobenzamide with lithium hydride in ether at −60°C for 15 min gave benzonitrile (30%) and benzylamine (8%); [114] and from 2-thiohomophthalimide and 5-methyl-2-thiohomophthalimide have been obtained 1,2,3,4-tetrahydroisoquinoline (40%, as the picrate) and 1,2,3,4-tetrahydro-6-methylisoquinoline (40%, as the picrate) respectively [37].

3. Electrolytic Reduction of Thioamides

Solutions in hydrochloric and sulphuric acids are used for the electrolytic reduction of thioamides. With relatively dilute acids amines are usually formed, but in concentrated acids (80% sulphuric acid) predominant formation of aldehydes occurs.

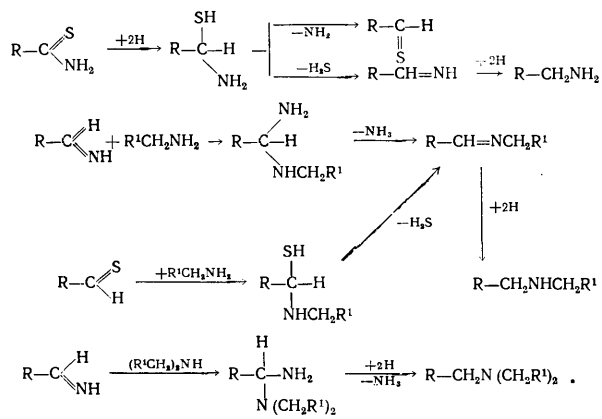
Phenylthioacetamide is reduced in solution in alcohol and hydrochloric acid to phenethylamine; *NN*-dimethylthiobenzamide in 60% sulphuric acid gives the corresponding tertiary amine in 75–100% yield; and *N*-alkylthioamides are reduced to secondary amines [146]. When, however, *NN*-dimethylthiobenzamide was reduced in 80% sulphuric acid, benzaldehyde (40%) was obtained together with small quantities of dimethylamine and benzyldimethylamine [112,113,149].

¶Thiobenzamide is converted into benzaldehyde also by the action of zinc and caustic potash (yield 42%). [147]

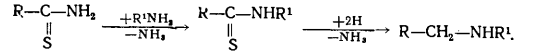
4. Reduction of Thioamides with Metal Amalgams

Aluminium and sodium amalgams are used for the reduction of thioamides, with ether and ethanol as solvents. The amalgams are added to the reaction mixture slowly and in slight excess. The reduction products are primary and secondary amines [146], their relative proportions depending on the thioamide. The reduction of thiobenzamide with an amalgam in moist ether yields benzylamine (85%) and dibenzylamine (8%); but when phenylthioacetamide was reduced under these conditions the products were phenethylamine and diphenethylamine in yields of 26% and 66% respectively [149].

Different products are formed if reduction takes place in the presence of an amine [146]. In the presence of ethylamine, for example, phenylthioacetamide yields a mixture of phenethylamine, diphenethylamine, and *N*-ethylphenethylamine. The thioamide is probably reduced initially to an α-amino-thiol, from which hydrogen sulphide splits off to form an aldimine. The latter is either reduced further to a primary amine or added to a primary or a secondary amine to form a secondary or a tertiary amine respectively. Formation of the various products can be represented by the schemes

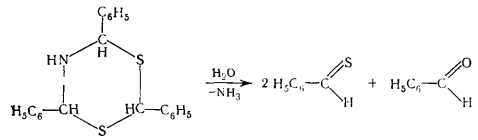


The formation of secondary amines can be explained by transamidation of the thioamide and reduction of the *N*-substituted thioamide:



Sodium amalgam has been used to reduce phenylthioacetamide and thiobenzamide in alcoholic solution [26,150]. Phenylthioacetamide gave a small quantity of 2-phenethylamine, but the main product was a solid, probably 2,4,6-tribenzyl-5,6-dihydro-1,3,5-dithiazine. The principal reduction product of thiobenzamide was thiobenzaldehyde; small quantities of benzylamine, benzonitrile, and benzaldehyde were also isolated. In this case it is assumed that 5,6-dihydro-2,4,6-triphenyl-1,3,5-dithiazine is an intermediate reduction product, hydrolysis of which

yields benzaldehyde and thiobenzaldehyde [150]:



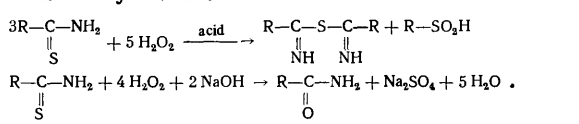
N-Substituted thioamides are reduced by sodium amalgam initially to the corresponding amines, after which other products are formed as a result of secondary reactions, as has been shown above [146].

VI. OXIDATION OF THIOAMIDES

The great variety of oxidising agents—hydrogen peroxide, acid hydroperoxides, nitrous, nitric, and sulphuric acids, halogens, hexacyanoferrates(III), potassium permanganate, ozone, metal oxides, alkene oxides, and other oxidants—have been used for oxidising thioamides.

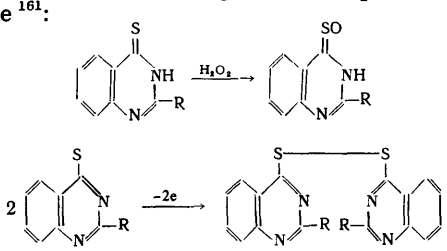
1. Oxidation of Thioamides by Hydrogen Peroxide and Hydroperoxides of Acids

The reaction between thioamides and hydrogen peroxide is conducted under acid, neutral, or alkaline conditions. In acid and neutral media disulphides, sulphinic acids, and other products depending on structure of the thioamides, but in alkaline medium the corresponding oxo-compound is always formed [37,151-155]:



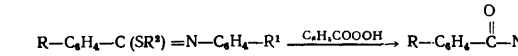
For example, thiobenzamide is oxidised by hydrogen peroxide in aqueous alkali to benzamide [151]; disulphides are not formed by this method of oxidation [153]. The oxidation of thioamides in alkaline medium takes place at low temperatures, its rate depending on the concentration of hydroxide ions. The reaction is used for the quantitative determination of sulphur in thioamides [151,156,157]. The oxidation of thioamides has been studied in detail [12,97,151-160].

Dihydroquinazoline-4-thione on oxidation with hydrogen peroxide in neutral medium gives the sulphoxide and the disulphide [161]:

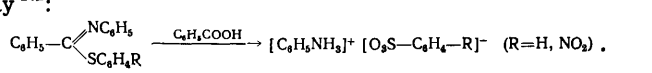


The oxidation of unsubstituted and mono- and di-*N*-substituted thioamides by hydrogen peroxide in neutral and weakly alkaline media (water, methanol to which pyridine has been added, or pyridine itself) often gives rise to *S*-oxides of thioamides [155,162-171] which are more stable than the thioamides themselves [162].

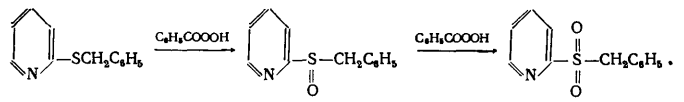
When isothioamides are oxidised with perbenzoic acid in chloroform, anilides are obtained [172]:



Sometimes anilinium sulphonates are obtained in this way [172]:

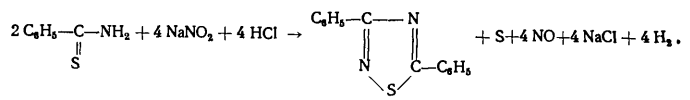


Sulphoxides [and sulphones] are other possible products [172]:



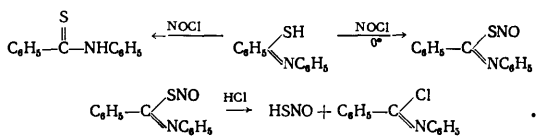
2. Oxidation of Thioamides by Nitrogen Compounds

Various compounds of nitrogen (nitric and nitrous acids, nitrosyl chloride, nitrogen dioxide, pentyl nitrite, etc.) are used, the nature of the products depending on the oxidant and the thioamide. If a solution of sodium nitrite is added to a solution of thiobenzamide in a mixture of ethanol and hydrochloric acid, the thiobenzamide is oxidised to 3,5-diphenyl-1,2,4-thiadiazole [45]:

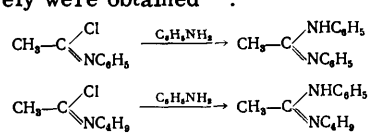


The same product is formed (in 75% yield) by the oxidation of thiobenzamide with nitric acid in acidic aqueous and non-aqueous media [173].

The oxidation of thiobenzanilide by nitrosyl chloride in ethereal solution in an atmosphere of nitrogen in the cold gives *N*-phenylbenzimidoyl chloride (yield 44%) and benzanilide [174]. It is assumed that an *S*-nitroso-derivative is formed as an intermediate:



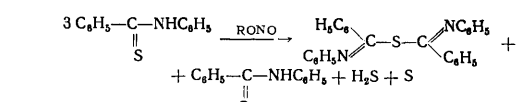
When thioacetanilide and *N*-butylthioacetamide were subjected to the same treatment with nitrosyl chloride, the imidoyl chlorides could not be isolated owing to their instability. However, their formation was proved by the action of excess of aniline on the reaction mixture, when *NN'*-diphenylacetamidine and *N'*-butyl-*N*-phenylacetamidine respectively were obtained [174]:



In pyridine oxidation of thiobenzanilide by nitrosyl chloride takes a different course: the oxidation products are di-*N*-phenylbenzimidoyl sulphide $C_6H_5.C(:N.C_6H_5).S.C(:N.C_6H_5).C_6H_5$ and an oily product; the latter decomposes slowly into sulphur and a sulphide [174].

With nitric oxide in ether in the cold *N*-butylthioacetamide gives *N*-butyl-*N*-nitrosoacetamide [174].

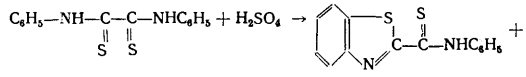
The reaction of thiobenzanilide with pentyl nitrite and ethyl nitrite at 0°C yielded after 2 days benzanilide and di-*N*-phenylbenzimidoyl sulphide [174]:



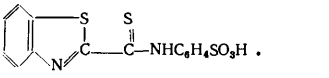
where $R = C_5H_{11}$, C_2H_5.

3. Oxidation of Thioamides by Sulphuric Acid

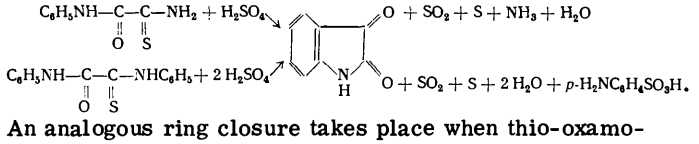
The oxidation of thioamides by sulphuric acid is used to obtain benzothiazole, isatin, and indole derivatives. The action of oleum or concentrated sulphuric acid on dithiooxanilide at room temperature gives a quantitative yield of benzothiazole-2-carbothioanilide [31]:



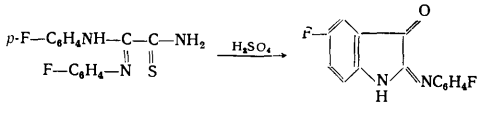
On being warmed with sulphuric acid this product is sulphonated to give



When oxanilothioamide or monothio-oxanilide is heated with 95% sulphuric acid until sulphur dioxide ceases to be evolved, isatin is obtained in 25% yield [31]:

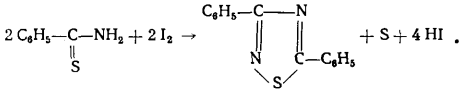


An analogous ring closure takes place when thio-oxamo-*NN'*-di-*p*-fluorophenylamidine is oxidised with sulphuric acid to give an indole derivative [175]:



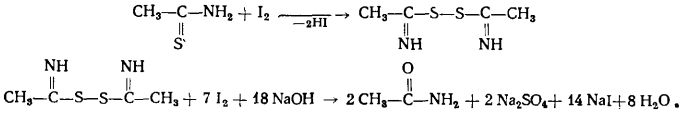
4. Oxidation of Thioamides by Halogens

On treatment with excess of iodine in alcoholic solution thiobenzamide undergoes condensation with elimination of a sulphur atom and formation of 3,5-diphenyl-1,2,4-thiadiazole [176]:



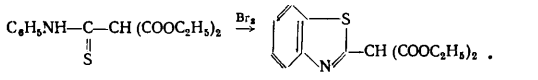
This product has previously been regarded as the isomeric 2,5-diphenyl-1,3,4-thiadiazole [26]. The reaction is probably common to thioamides in which the nitrogen atom is unsubstituted. According to the early results thiobenzamide is not oxidised by iodine [69,174].

In alkaline solution thioamides are oxidised by iodine to amides [157]. This reaction is used for the quantitative determination of thioamides. With thioacetamide the reaction can be expressed by the equations [157]

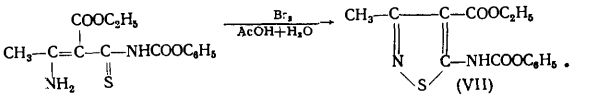


The intermediate disulphide has been isolated only when the thioamide is oxidised by iodine in a mineral acid. Bromine or a mixture of potassium bromide and bromite can be used instead of iodine in acid medium. Dithiooxamides are oxidised by iodine in acid medium better than is thioacetamide.

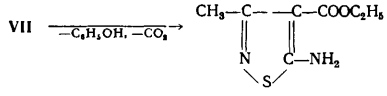
The oxidation of thioanilides by bromine in formic or acetic acid yields benzothiazoles [8,177,178]:



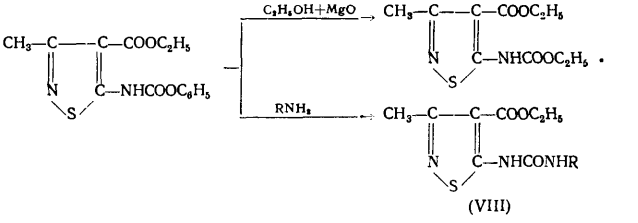
Phenyl 4-ethoxycarbonyl-3-methylisothiazol-5-ylcarbamate (VII) has been obtained in this way [179]:



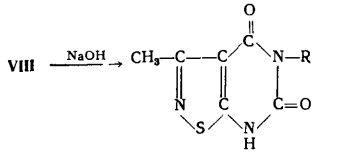
When (VII) is treated with a weak base, or when it is boiled in aqueous dimethylformamide for a long time, phenol and carbon dioxide are split off with formation of the amine:



Other nucleophilic reagents will remove only the phenoxy-group from (VII):



The latter compound can be cyclised on heating to form isothiazolo[5,4-*d*]pyrimidines:



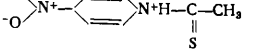
where R = H, CH_3, C_6H_5, OH, NH_2.

Isothiazoles are products of the oxidation of thioamides by bromine in acetic acid and in other cases [8,180–183].

5. Oxidation of Thioamides by Hexacyanoferrates(III)

The oxidation of thioacetanilide and thiobenzanilide derivatives by means of potassium hexacyanoferrate(III) in alkaline aqueous solution involves cyclisation with the formation of benzothiazole derivatives (Jacobson's method) [184]. Thioacetanilide derivatives yield 2-methylbenzothiazole derivatives, ease of cyclisation being affected by the nature of the substituent (methoxyl, methyl, chloro, nitro), its position in the anilide ring, and the solubility of the thioacetanilide derivative in the alkaline solution [185–187]†. Thus the yield of 2-methylbenzothiazole

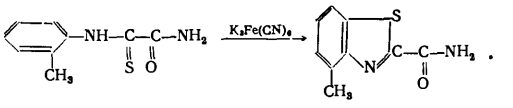
†*p*-Nitrothioacetanilides are unable to form 2-methyl-6-nitrobenzothiazole. This is explained by the existence of the isomeric structure



in which thiol–enolisation [sic], and hence also ring closure, are difficult. In this case oxidation results in the formation of a 50% yield of *p*-nitroacetanilide [186].

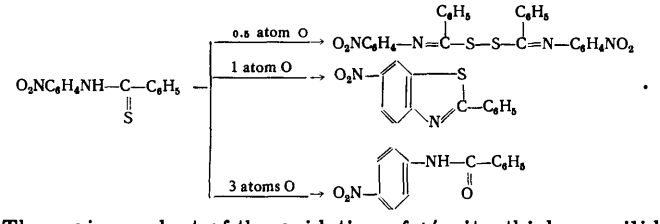
increases as the solubility of thioacetanilide increases with rise in the sodium hydroxide concentration to 2 *N*, after which it falls appreciably [186].

Various derivatives of thio-oxanilic acid are easily cyclised to benzothiazoles under the influence of potassium hexacyanoferrate(III):



If a large excess of the ferricyanide is taken, the reaction is complete in 10 min [82].

Sometimes cyclisation does not occur on the oxidation of thioanilides by potassium hexacyanoferrate(III) in alkaline solution, other products being formed [188]:

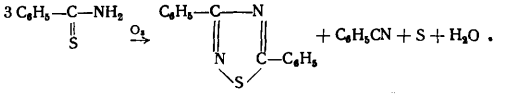


The main product of the oxidation of *p'*-nitrothiobenzanilide in cold alkaline solution was a derivative of dibenzimidoyl disulphide [189], and in hot alkali the main product was *p'*-nitrobenzanilide. In both cases the yield of 6-nitro-2-phenylbenzothiazole was small [186,189,190].

The action of potassium hexacyanoferrate(III) in alkaline solution sometimes converts a thioamide into a nitrile and an oxamide [82]. Thio-oxanilonitrile $C_6H_5.NH.CS.CN$ and thio-oxanilamide $C_6H_5.NH.CS.CO.NH_2$ have been obtained by treating *N*-phenyldithio-oxamide with a quantity of the oxidant corresponding to 1 atom of oxygen, when 75% of the thioamide is converted into the nitrile, and 25% into the oxamide. Although thio-oxanilamide can be obtained by heating thio-oxanilonitrile in alkaline solution, it is more probably directly from the phenyldithio-oxamide [82].

6. Other Methods for the Oxidation of Thioamides

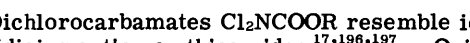
Thioamides are oxidised by ozone in inert anhydrous solvents, e.g. benzene and carbon tetrachloride. Thiobenzamide is converted into *N*-benzimidoylthiobenzamide $C_6H_5.C(:NH).NH.CS.C_6H_5$, which is then cyclised to 3,5-diphenyl-1,2,4-thiadiazole [191]:



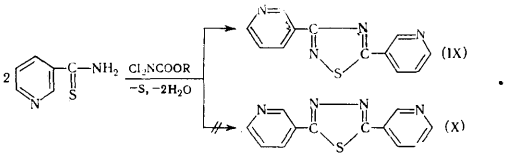
Other products of the reaction are benzonitrile and sulphur [192]. Thio-*p*-toluamide behaves similarly, but thioacetanilide is converted into acetanilide and resinous products. The corresponding amides and nitriles have been obtained also by the action of ozone on unsubstituted thiobenzamide in aqueous medium. The reaction between thioacetamide and ozone in benzene or water, on the other hand, yields acetic and sulphuric acids, ammonia, and sulphur.

Dithiocamphorimide is oxidised by potassium permanganate to camphorimide [102].

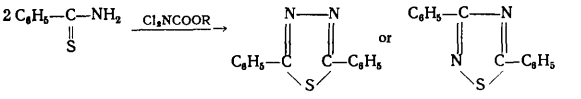
The oxidation of thioamides by selenium dioxide (in alcoholic solution) yields the corresponding amides and selenium trisulphide [159,193-195]. The oxidation of *N*-benzylthiobenzamide gives the amide only when more than 2 moles of the thioamide are taken per mole of selenium dioxide. With equimolecular proportions of the reactants oxidation is accompanied by cleavage of the carbon–nitrogen bond [194]:



NN-Dichlorocarbamates Cl_2NCOOR resemble iodine in their oxidising action on thioamides [17,196,197]. Oxidation is usually conducted in an aqueous suspension of the reactants containing a slight excess of the dichlorocarbamate. Nicotinothioamide is oxidised to 3,5-dipyrid-3'-yl-1,2,4-thiadiazole (IX), not the isomeric 1,3,4-thiadiazole (X):[195]



In the case of thiobenzamide it has not been established whether the oxidation product is a 2,5-disubstituted 1,3,4-thiadiazole or a 3,5-disubstituted 1,2,4-thiadiazole [195]:

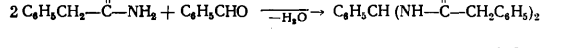


Thioamides can be oxidised also by alkene oxides and certain esters. Thus boiling a solution of thioacetamide in methanol with cyclohexene oxide for 5 h gave acetamide (85%) and a sulphur-containing residue [198]. When thiobenzamide was oxidised by the ethyl ester of phenylglycine $C_6H_5.NH.CH_2.COOC_2H_5$, the products were benzamide, ethyl cinnamate, and sulphur.

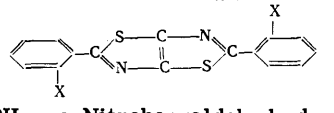
The oxidation of thioamides by sodium *o*-hydroxymercuribenzoate $HOHgC_6H_4COONa$ is used for the analytical determination of thioamides [199,200]. Certain *N*-monoarylthioamides are not determined by this method [200].

VII. REACTIONS OF THIOAMIDES WITH ALDEHYDES AND KETONES

Phenylthioacetamide reacts with benzaldehyde to form an oily product:

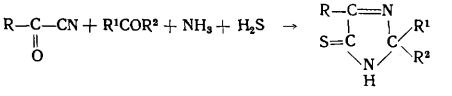


which gives a solid salt with platinum(II) chloride [150]. The reaction of dithio-oxamide with benzaldehyde and salicylaldehyde [201] is accompanied by dehydrogenation and the formation of thiazolothiazole derivatives [202]:

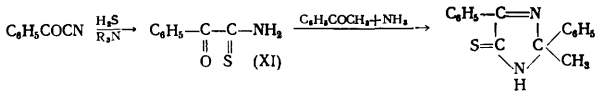


where X = H, OH. *o*-Nitrobenzaldehyde does not react [202].

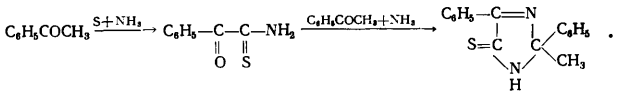
Nor could individual products be isolated from the reaction of thioamides with aliphatic aldehydes and aryl methyl ketones. Acyl cyanides (aromatic and aliphatic) react with ketones in the presence of hydrogen sulphide and ammonia to form substituted Δ^3-imidazoline-5-thiones [203,204]:



α-oxo-thioamides being formed from the acyl cyanide as intermediate products. The action of hydrogen sulphide on benzoyl cyanide in the presence of a tertiary amine in an aprotic solvent gives an excellent yield of the thioamide of phenylglyoxylic acid (XI), which on reaction with acetophenone and ammonia for a few minutes is converted quantitatively into 2-methyl-2,4-diphenyl-Δ^3-imidazoline-5-thione:

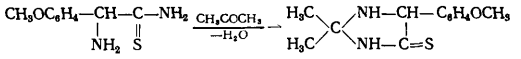


Imidazoline-5-thione derivatives are formed also by the action of elementary sulphur and ammonia on ketones [205]. Reaction between a thioamide and a ketone is assumed to underlie the synthesis of a Δ^3-imidazoline-5-thione by the action of excess of ammonia and sulphur on acetophenone [204,206]:

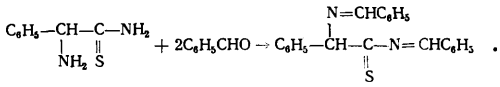


Other Δ^3-imidazoline-5-thiones have been obtained similarly.

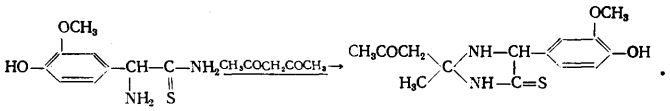
When α-amino-thioamides are boiled in absolute alcohol with equimolecular quantities of aliphatic [207] or aromatic [208] aldehydes, ketones [209], and αγ-dioxo-compounds [210], 2,2-disubstituted imidazolidine-4-thiones are formed in good yield:



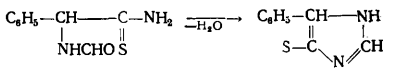
If two equivalents of the oxo-compound are used, heterocycles are not formed [207]:



It is probable that only one oxo-group is involved in the interaction of equimolecular quantities of a thioamide and pentane-2,4-dione, since imidazolidine-4-thiones—not methylenebis-2-imidazolidine-4-thiones—are formed [211]:

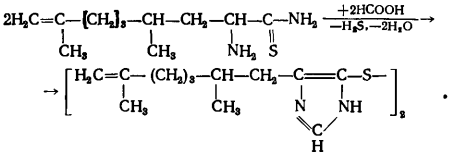


Imidazoline-4-thiones are obtained also by the cyclisation of α-amido-thioamides‡ when boiled in alcoholic solution in the presence of an acid or a base [212-214]:



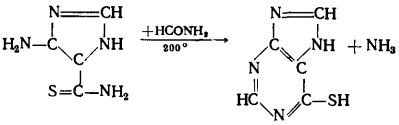
‡The intermediate α-amido-thioamides were obtained by treating α-amino-thioamides with formic acid in the absence of a solvent [207], or by the action of acetic anhydride (1–2 equivalent) or benzoyl chloride on the α-amino-thioamide [33,208]. In this way α-formamide, α-acetamide, or α-benzamide derivatives were obtained; the yields of the latter compounds were low.

When 2-amino-4,8-dimethylnon-8-enothioamide is heated with formic acid the resulting imidazolinethione is oxidised to the disulphide [213]:



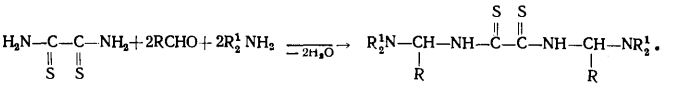
Disulphides are formed also by the oxidation of imidazolinethiones by hydrogen peroxide or iodine.

Cyclic amino-thioamides also react with aldehydes. Thus 4-amino-Δ^2-imidazoline-5-carbothiamide and formamide yield purine-6-thiol [215]:



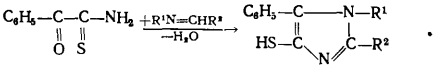
Phenanthraquinone also undergoes this reaction.

The reaction of dithio-oxamide (or an *NN'*-dialkyldithio-oxamide) with a solution of an aldehyde and a secondary amine in chloroform involves condensation of the three reactants [216]:



Benzaldehyde and several aliphatic aldehydes have been used together with dialkylamines, piperidine, and alkylarylamines in this reaction.

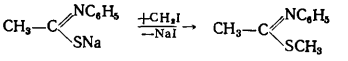
Phenylglyoxylthioamide reacts with aldimines (in benzene at 45°C for 2 h) to form 4-mercapto-5-phenylimidazoles [6]:



Primary amines do not undergo this reaction, since the addition product of a primary amine and an aldehyde immediately eliminates water, and the resulting Schiff base does not react with dithio-oxamide. Nor do dithio-oxanilides undergo this reaction; tetra-substituted dithio-oxamides form unstable compounds, which decompose into their components [216]. These products are oils in the case of the reaction of tetra-substituted dithio-oxamides with formamide and the lower dialkylamines, and crystalline solids in other cases.

VIII. REACTIONS OF THIOAMIDES WITH ALKYL HALIDES AND HALOGENATED AMINES, KETONES, and ACIDS

Alkyl and aralkyl halides act on the sodium salts of thioamides to form isothioamides, which are usually prepared in this way. Thus methylated *N*-phenylthioacetamide was first obtained by the action of methyl iodide on the sodium salt of thioacetanilide [217]:



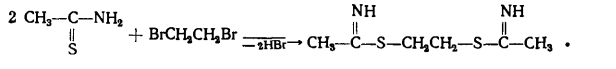
the solvent being ethanol. Heating *N*-benzylthioacetamide in methyl iodide gives a quantitative yield of the hydriodide of S-methyl *N*-benzylthioacetimidate [218]; on treatment with

caustic potash the free base $CH_3.C(:N.CH_2.C_6H_5).S.CH_3$ was isolated in 64% yield§.

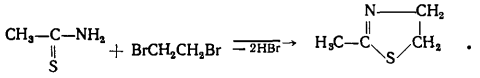
Unsubstituted thioamides also react with the lower alkyl halides to form salts of isothioamides [219]. Equimolecular quantities of the alkyl halide and the thioamide are usually taken, and the reaction is conducted in dry acetone. Propyl and butyl iodides hardly react even when boiled for 2 h.

The sodium and potassium salts of *N*-benzylthioamides react with alkyl halides in xylene solution to form products $C_6H_5.C(SR):N.CH_2.C_6H_5$ in 45–65% yields [159]. The action of alkyl halides on *NN'*-disubstituted thioamides gives salts to which the structure $[R.S.CR^2:NR_2^1]^+X^-$ is assigned [60].

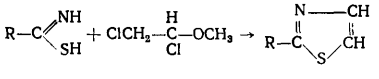
Reaction between dibromoethane and thioamides involves cyclisation with the formation of 2-thiazoles [184], and *N*-arylthioamides yield *N*-aryl-2-thiazole salts. Cyclisation is accompanied by bis-*S*-alkylation. Temperature has a substantial effect on the course of the reaction. Thus thioacetamide reacts with dibromoethane at 100°C to form ethylene diacetimidothioate [47]:



But at the boiling point of dibromoethane (131°C) 2-methyl-Δ^2-thiazoline is formed in low yield [220]:

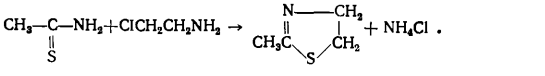


Thiazole and 2-methylthiazole have been obtained in good yield by treating thioformamide and thioacetamide respectively with an aqueous solution of 1,2-dichloroethyl methyl ether at 60°C:



where R = H, CH_3.

Another general method for obtaining Δ^2-thiazolines is the reaction between thioamides and β-halogenated amines. When, for example, thioacetamide is boiled with 2-chloroethylamine for 2 h, at 32.3% yield of 2-methyl-Δ^2-thiazoline is obtained [222]:



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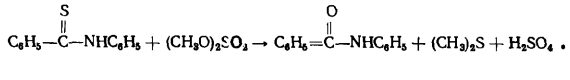
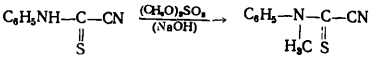
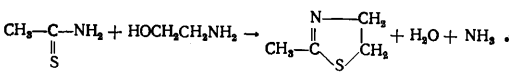
§ Dialkyl sulphates react differently with thioamides. In dry inert solvents dimethyl sulphate does not react with thioamides. In the presence of small quantities of water the process goes as follows [103]:



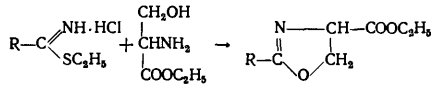
However, alkylation in aqueous alkali yields *N*-alkylated thioamides. For example, thio-oxanilonitrile reacts with dimethyl sulphate in 20% aqueous alkali to form the *N*-methylated product [104]:



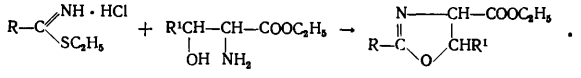
2-Aminoethanol reacts similarly:



Esters of β-hydroxy-α-amino-acids react with salts of isothioamides to form oxazolines. Thus ethyl 2-alkyl- and 2-aryl-oxazoline-4-carboxylates are easily obtained from the ethyl ester of serine:

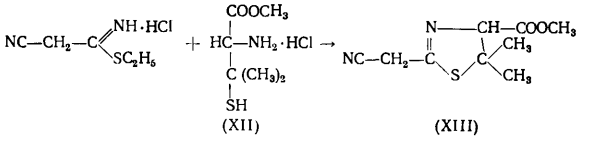


Application of this reaction to derivatives of serine gives 5-substituted oxazoline derivatives [223,224]:

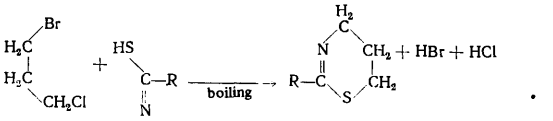


The yield of oxazolines improves substantially as the molecular weight of the ester group in the serine increases from methyl to propyl [223].

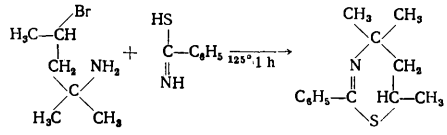
Esters of β-mercapto-α-amino-acids, in contrast to β-hydroxy-α-amino-carboxylic esters, react with thioamides [225,226] to form thiazoles. Thus the ester of penicillamine (XII) and the hydrochloride of ethyl cyanothioacetimidate react in dry chloroform to produce the 2-cyanomethyl-5,5-dimethylthiazoline-4-carboxylic ester (XIII):[227,228]



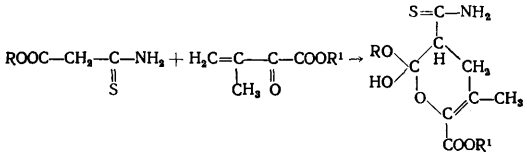
1-Bromo-3-chloropropane reacts with thioamides to form the 2-substituted 5,6-dihydro-1,3-thiazines:



The yields are often theoretical, but only 10% in the case of thioacetamide. 5,6-Dihydro-1,3-thiazines are obtained also by the reaction of thioamides with γ-halogeno-amines:



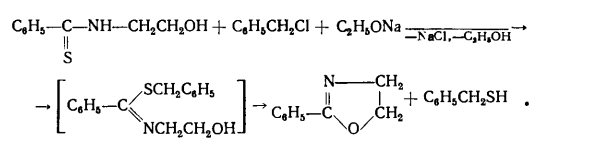
Another method of obtaining Δ^2-dihydrothiazines is the reaction between α-thiocarbamoylacetic esters and vinylglyoxylic esters:



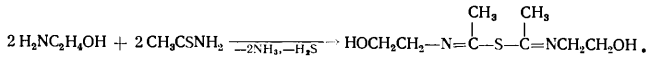
where R = CH_3, $C_6H_5CH_2$, $(CH_3)_3C$. The reaction goes smoothly in neutral medium at room temperature [229].

Reviews have been published [184,230,231] on the synthesis of thiazoles, Δ^2-thiazolines, and 5,6-dihydro-1,3(or 4)thiazines, which include this method. A modification of the method is the preparation of Δ^2-thiazolines by treating *N*-2-hydroxyalkyl-amides with phosphorus pentasulphide [184,232]. Thus *N*-2-hydroxyethylbenzamide gives a 68% yield of 2-phenyl-Δ^2-thiazoline [233-237]. Thioamides are assumed to be formed as intermediates [238].

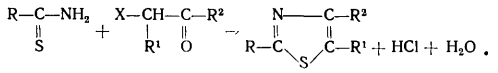
When *N*-2-hydroxyethylbenzothioamide is boiled with sodium ethoxide and benzyl chloride in ethanol (these conditions are usual for the *S*-alkylation of thioamides), 2-phenyloxazoline [111] and phenylmethanethiol [59] are obtained:



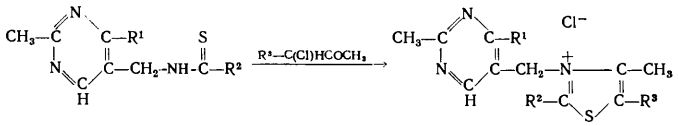
It is assumed that *S*-benzyl *N*-2-hydroxyethylthiobenzimidate is formed initially, and then undergoes cyclisation. Aminoethanol is able also to react differently with thioamides from the way mentioned above [70]. When an equimolecular mixture of this amine and thioacetamide is heated at 75°C, two molecules of each reactant undergo condensation with the evolution of two molecules of ammonia and one molecule of hydrogen sulphide, a sulphide being formed:



Thiazoles can be obtained also by the reaction of thioamides with α-halogeno-ketones and -aldehydes [9,184,239,240]:

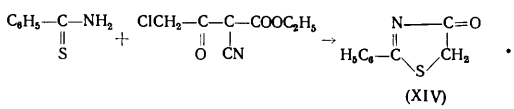


N-Substituted thioamides, e.g. 4-amino-5-thioformamidomethylpyrimidine [241], are converted into the corresponding *N*-substituted thiazoles [76,242-251]:



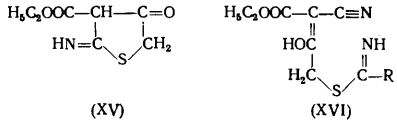
where $R^1 = NH_2$ and $R^2 = R^3 = H$.

When thiobenzamide is heated with γ-chloro-α-cyanoacetoacetic ester in aqueous ethanol for several days, 4-oxo-2-phenyl-Δ^2-thiazoline (XIV) is formed in 75% yield [252]:



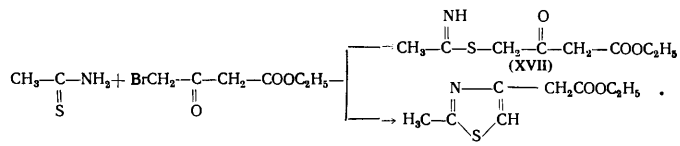
(XIV)

Under these conditions thioacetamide yielded two products



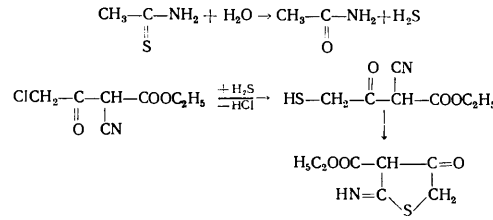
(XV) (XVI)

ethyl 2-imino-4-oxothiolan-3-carboxylate (XV) and a small quantity of a compound $C_7H_7NO_2S$, whose structure was not established. It is assumed that (XV) is formed by cyclisation of the intermediate product (XVI: R = C_6H_5). This hypothesis is based on the formation of ethyl 2-methylthiazol-4-ylacetate when thioacetamide is boiled with ethyl γ-bromoacetoacetate for 30 min and allowed to stand for a long time [253]:

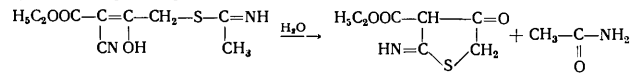


(XVII)

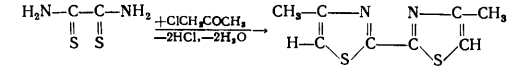
If the reaction is halted and rapid crystallisation is effected, ethyl γ-acetimidoylthioacetoacetate (XVII) is formed [253]. After isolation the latter does not give thiazole derivatives under various reaction conditions. If R = C_6H_5 in (XVI), the mobility of the imino-proton is increased, and favourable conditions are created for ring closure and the formation of (XIV). [252] If, however, R = CH_3, the nitrogen-hydrogen bond becomes more stable, and cyclisation does not occur. Since this hypothesis does not explain the formation of (XV), the reaction scheme



has been suggested. Another explanation of the formation of (XV) is hydrolysis of (XVI: R = CH_3).

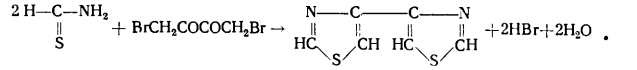


Dithio-oxamides react with α-halogeno-ketones to form bithiazolyls. Thus 4,4′-dimethyl-2,2′-bithiazolyl is readily formed from dithio-oxamide and chloroacetone in alcoholic solution [254]:

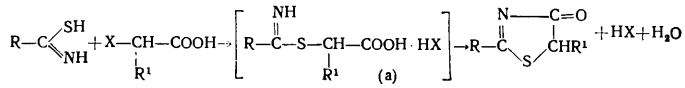


The action of dithio-oxamide on 1,4-dibromobutane-2,3-dione results in the rapid formation of brown polymeric products of high melting point (probably polythiazolines [254]), which are practically insoluble in almost all solvents. Polymeric products are obtained also by the reaction of 1,4-dibromobutane-2,3-dione with dithioterephthalamide and dithiomalonamide [255,256].

Thioformamide gives 4,4′-bithiazolyl when warmed with 1,4-dibromobutane-2,3-dione in alcohol [257]:

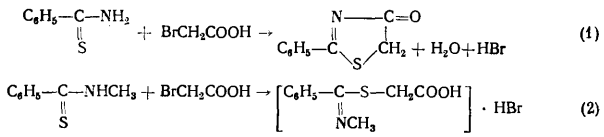


α-Halogeno-carboxylic acids react with thioamides to form 4-oxothiazolines [184,258]. 2-Alkylated and 2-arylated derivatives are obtained from aliphatic and aromatic thioamides [196]:

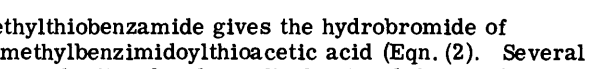


where R = Alk or Ar. Equimolecular quantities of the reactants are usually boiled in water or in toluene. Reaction is slow. An isothioamide salt (a) is formed as the first stage [196]. In some cases (e.g. with α-bromoisobutyric acid) the intermediate isothioamides do not undergo cyclisation.

Thioamides in which the nitrogen atom is not substituted react with bromoacetic acid to form 4-oxothiazolines, whereas *N*-substituted thioamides yield acyclic "isothioamides":[77]

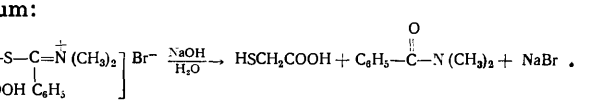


(1)

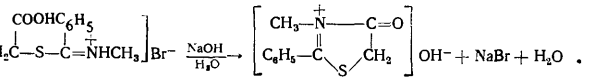


(2)

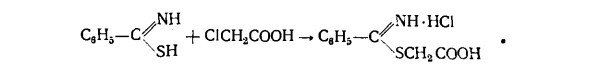
N-Methylthiobenzamide gives the hydrobromide of α-*N*-methylbenzimidoylthioacetic acid (Eqn. (2). Several other *N*-substituted and *NN*-disubstituted thioamides react similarly. *N*-α-Carboxymethylthiobenzylidene-*NN*-dimethylammonium bromide is hydrolysed in alkaline medium:



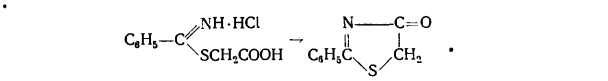
But if the imino-group is incompletely substituted, cyclisation occurs:



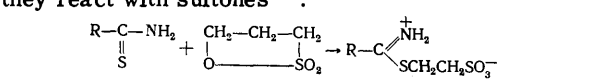
In acid media *N*-monosubstituted thiobenzimidates also give 4-oxothiazolines, whereas *NN*-disubstituted thiobenzimidates yield isothioamides. With chloroacetic acid thiobenzamide forms initially an alkylation product[197,259]:



When heated to 100°C or in the presence of a condensing agent, e.g. acetic anhydride, this gives a 4-oxothiazoline[258]:

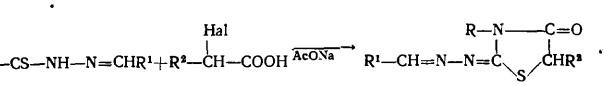


This reaction usually occurs more rapidly and under more moderate conditions with derivatives of aliphatic thioamides. *S*-Alkylation of thioamides is observed also when they react with sultones[259]:

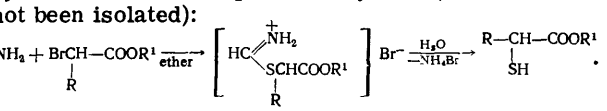


where R = CH_3, C_6H_5, *o*- and *p*-$CH_3C_6H_4$. The reaction is accomplished by boiling in benzene for 1 h. With aromatic thioamides the yield reached ~ 80%.

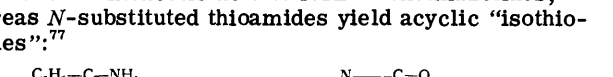
α-Halogenated carboxylic acids react also with thiosemicarbazones in the presence of fused sodium acetate. Cyclisation takes place with the formation of 5-alkyl(or aryl)-2-alkylidenehydrazono-3-aryl-4-oxothiazolidines[260-262]:



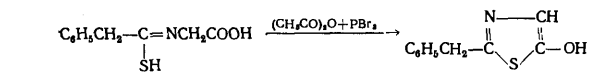
Thioformamide differs from other thioamides in its reaction with α-halogenated carboxylic acids[263]. Thus with α-halogeno-carboxylic esters 50–80% yields of α-mercapto-carboxylic esters are obtained. When the reaction is conducted in ether, salts of α-formimidoylthioalkanoic esters are formed initially, and are easily hydrolysed to the α-mercapto-carboxylates (thiazolones have not been isolated):



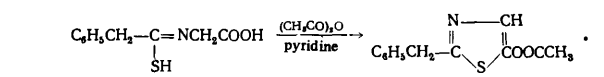
Diethyl dibromomalonate oxidises thioformamide under these conditions:



N-Carboxymethylthioamides R.CS.NH.CH_2.COOH, either as such or as intermediate products at the instant of isolation, are used to obtain thiazole and oxazole derivatives. For example, the action of acetic anhydride and phosphorus tribromide on *N*-α-mercaptophenethylideneaminoacetic acid yields 2-benzyl-5-hydroxythiazole[264]:

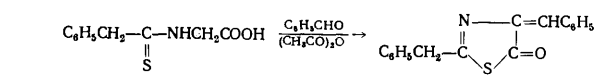


When acetic anhydride and pyridine are used, 2-benzylthiazol-5-yl acetate is formed:

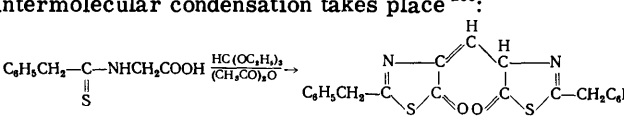


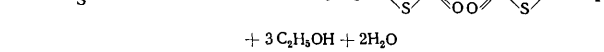
Similarly, 5-ethoxy-2-methylthiazole is obtained by heating the ethyl ester of *N*-acetylglycine with phosphorus pentasulphide[265].

2-Benzyl-4-benzylidene-5-oxothiazoline is formed when thiophenaceturic acid [phenylthioacetylglycine] is treated with acetic anhydride in the presence of benzaldehyde[266]:

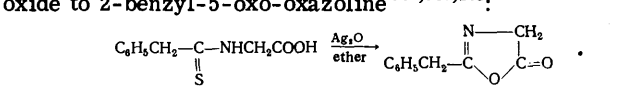


When benzaldehyde is replaced by ethyl orthoformate, intermolecular condensation takes place[266]:

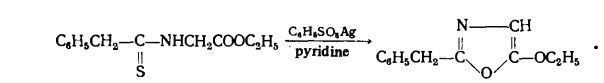




5-Oxazolones are formed by the treatment of an *N*-carboxymethylthioamide with a silver salt or oxide[267]. In dry ether thiophenaceturic acid is cyclised by silver oxide to 2-benzyl-5-oxo-oxazoline[264,267,268]:

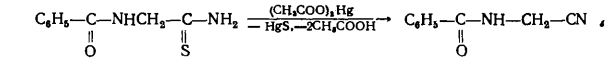


2-Benzyl-5-ethoxyoxazole is formed by treating ethyl thiophenaceturate with silver benzenesulphonate in cold pyridine[269]:

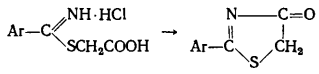


The free acid reacts similarly[61,270].

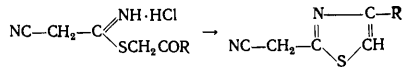
Thioamides in which the nitrogen atom is unsubstituted react with silver salts or the oxide, usually with formation of the corresponding nitrile and precipitation of silver sulphide. When equimolecular quantities of the thioamide of hippuric acid and mercury(II) acetate are mixed, mercury(II) sulphide is precipitated, and hippuronitrile remains in solution[270]:



Aromatic imidate derivatives of thioglycollic acid [271] and its esters [272] form 2-substituted 4-oxothiazolines when boiled in toluene:

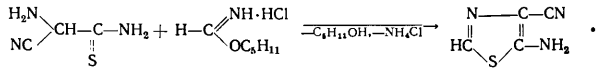


4-Methyl- and 4-phenyl-thiazoles are formed similarly [272]:



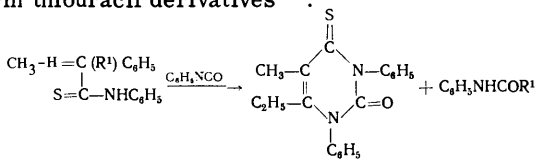
where R = CH_3, C_6H_5.

The thioamide of α-cyanoglycine reacts with isopentyl formimidate to give aminothiazole:



Other formimidates and salts of thioformimidates, however, do not yield definite products [273].

Aminoalkenothioanilides react with phenyl isocyanates to form thiouracil derivatives [274]:



Oxidation of these products by hydrogen peroxide replaces the sulphur by oxygen.

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Stereochemistry of the Cathodic Reduction of Halogenated Organic Derivatives

K.P.Butin

Investigations on the stereochemistry of the electrochemical reduction of organic halogeno-derivatives are reviewed, and a comparison is made of the behaviour of these compounds on mercury and on platinum. Specific interaction between the halogen and the mercury electrode is shown to occur during reduction: i.e. direct contact between the halogeno-derivative and mercury is a condition for production of the transition state. In the reduction of optically active halogenocyclopropanes electron transfer occurs from the halogen atom with formation of a carbanion having the same configuration as the original halogeno-compound, but subsequent reactions (protonation, inversion, sp^3–sp^2 transition, etc.) may have a substantial effect on the configuration of the final product. The simultaneous detachment of two halide anions in the reduction of vicinal dihalogeno-derivatives results in the formation of compounds containing multiple bonds. A list of 40 references is included.

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I. INTRODUCTION

The electrochemical reduction of the carbon–halogen bond is a heterogeneous process occurring on the electrode surface. Therefore the behaviour of organic halogeno-derivatives during such reduction depends not only on their structure but also on the factors which distinguish heterogeneous from homogeneous processes. Among such factors are primarily (1) the orientation of the transition state in the field of the electrode—i.e. the positions of the atoms and the direction relative to the electrode surface of the dipoles of the bonds undergoing rupture—and (2) the distance from the electrode surface to the point at which the transition state is located, i.e. the length of the path traversed by the electrons from the surface to the molecule of the halogeno-derivative.

From investigations on the effect of solution composition (nature and concentration of electrolyte, nature of solvent, etc.) on the form of the polarisation curves it has been concluded that, in the cathodic reduction of organic compounds, the transition state is adsorbed on the electrode [1].

The present Review will examine the relation between the three-dimensional structure and the electrochemical properties of halogenated organic compounds.

Most monohalogeno-derivatives are reduced at a mercury cathode irreversibly in two stages, which correspond to the successive transfer of two electrons:

$$\begin{aligned} R{-}X + e^- &\xrightarrow{\text{slow}} I \quad \text{(intermediate cpd.)} \\ I + e^- &\xrightarrow{\text{rapid}} R^- + X^- \end{aligned} \qquad (1)$$

Transfer of the second electron is usually rapid, and therefore only one two-electron wave is observed on the polarogram. It is difficult to establish the nature of intermediate compound (I) formed by transfer of the first electron, but it may be assumed to be either a radical-anion $(R{-}X)^\bullet$ or a combination of a radical $R^\bullet$ and a halide anion. The carbanion R^- formed as a result of the two-electron transfer is in most cases a very strong base, and therefore rapidly detaches a proton from a molecule of the solvent (HS), being thus converted into a hydrocarbon:

$$R^- + HS \xrightarrow{\text{rapid}} RH + S^- \qquad (2)$$

The stereochemical result of the formation of a hydrocarbon from a halogeno-derivative may be determined either by the electron transfer (1) or by the protonation (2). If the carbanion formed by reaction (1) has insufficient time to lose its original configuration before capture of a proton, the stereochemistry of the reduction will be determined by the electrochemical stage (1). Apart from structural factors, the configurational stability of the primary carbanion R^- may be promoted also by its interaction with the electrode surface.

A change in the original configuration may occur also at the stage of formation of the intermediate compound I (Eqn. 1), provided that this compound includes the radical $R^\bullet$ (in the case of a radical-anion the configuration would probably be maintained). This possibility creates additional difficulties in interpreting the stereochemical results of the reduction of halogeno-derivatives. In order to reduce to a minimum the effect of isomerisation at the stage of transfer of the first electron, compounds which are reduced at fairly negative potentials must be chosen for investigation of the stereochemistry. In other words, the rate of transfer of the second electron, which depends on the potential, should exceed considerably the potential-independent rate of isomerisation of the radical $R^\bullet$ into the thermodynamically more advantageous configuration. This aspect will be discussed in greater detail in Section III.

The mechanism of the cathodic reduction of organic halogeno-derivatives has already been discussed in several reviews [2–4]. The stereochemistry of the electrochemical reactions of organic compounds forms the subject of a recently published Review [5]. Few papers have been published on the stereochemistry of the cathodic reduction of halogeno-derivatives, almost all during recent years.

II. ORIENTATION OF CARBON–HALOGEN DIPOLE IN THE FIELD OF THE ELECTRODE

Most organic halogeno-derivatives are reduced with a mercury electrode at potentials at which the electrode surface is negatively charged. However, this does not mean that the $R^{\delta+}-X^{\delta-}$ dipole is necessarily arranged with its positive pole towards the electrode surface and the negative pole in the solution. On the contrary, many data show that, when halogeno-derivatives are adsorbed on a negatively charged mercury surface, this dipole is directed with its negative pole towards the electrode[2]: i.e. an electrostatically disadvantageous orientation is established. The reason is that halogens have a specific affinity for mercury. If the Hg←XR interaction energy on formation of the transition state exceeds the change in electrostatic energy accompanying reorientation, an electrostatically unfavourable orientation is established.

In this connection it is interesting to compare the behaviour of halogeno-derivatives on mercury and platinum electrodes. According to Vlček[6] cobalt(III) complexes containing as ligands anions which form with mercury stable complexes or insoluble salts (Cl^-, Br^-, I^-, CNS^-, etc.) are reduced on mercury at abnormally positive potentials. The variation in the reduction potentials of these compounds does not correspond to their position in the corresponding "structural" series which includes complexes with other anions. On a platinum electrode, however, no abnormalities are observed, which indicates "catalysis by the surface of the mercury electrode"[6]. Interaction of the halogenated derivatives with the surface of metallic mercury may lead to the formation of organomercury compounds. In the reduction of allyl iodide, benzyl iodide[8], ethyl α-bromophenylacetate, and several other compounds, which may give relatively stable radicals R$^\cdot$, organomercury compounds are already formed on contact with the electrode surface. In these cases the polarograms of the halogeno-derivatives exhibit two one-electron waves which are identical with the waves of the corresponding organomercury compounds, e.g.

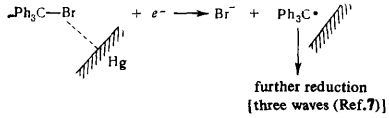
$$C_6H_5CH_2I + Hg \xrightarrow{\text{rapid}} C_6H_5CH_2HgI$$

$$C_6H_5CH_2HgI + e^- \rightarrow C_6H_5CH_2Hg^\cdot \quad (\text{or } C_6H_5CH_2^\cdot + Hg) \text{ (1st wave)}$$

$$C_6H_5CH_2Hg^\cdot + e^- + H^+ \rightarrow C_6H_5CH_3 + Hg \text{ (2nd wave)}$$

In most cases, however, the formation and reduction of organomercury compounds is merely a side-reaction accompanying the cathodic reduction of the halogeno-derivative and is due to interaction of RX with the electrode surface. Nevertheless, chloro-, bromo-, and iodo-derivatives of *o*-, *m*-, and *p*-barenes [1,2-, 1,7-, and 1,12-dicarbaclovododecaborane-12] are fairly easily reduced on mercury, the iodo-derivatives reacting the most readily, with reduction potentials close to the dissolution potentials of mercury. On platinum, however, these compounds are not reduced in the accessible potential range (to −1.8 V relative to the saturated calomel electrode, s.c.e. in anhydrous dimethylformamide. Diphenyliodonium salts behave similarly, being very easily reduced on mercury but not reduced on platinum[8–10].

Fig. 1 shows polarograms of triphenylbromomethane obtained on mercury and platinum electrodes in dimethylformamide. A "normal" two-electron wave is observed on platinum, whereas four waves are observed on mercury, the first of which is located at far less negative potentials †. This is probably due to interaction between the halogeno-derivative and mercury with formation of a triphenylmethyl radical[7]:



Similar phenomena are observed also with diphenylbromomethane and 9-bromofluorene.

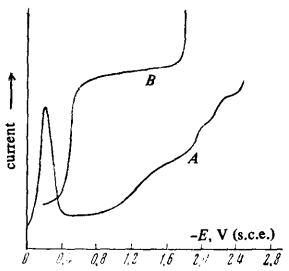


Figure 1. Polarograms for trimethylphenyl bromide in dimethylformamide containing 0.1 M tetraethylammonium bromide at 25°C on:
A) mercury; B) platinum.

These results confirm the earlier conclusion[11,12] that a transition complex involving the metal of the electrode surface is formed in the reduction of halogeno-derivatives. This means that the reducible molecule is tightly "clamped" to the electrode surface, the $R^{\delta+}-X^{\delta-}$ dipole being so arranged that the halogen atom is able to interact with the mercury. Such interaction is possible also with a "perpendicular" orientation of the dipole with its negative pole towards the electrode surface and with orientation parallel to the surface. The true orientation of the halogeno-derivative may be intermediate between these two extreme cases.

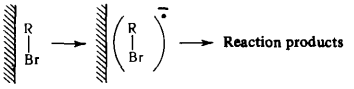
It has been found[13] with a large number of bromoalkanes RCH_2Br that the half-wave potentials do not correlate satisfactorily with the Taft σ^*-constants for the groups R. Correlation with the σ^*-constants of the groups RCH_2 is still less satisfactory. Substantial improvement is obtained by taking into account the steric hindrance due to the substituent R, i.e. by introducing the steric constants E_S into the correlation equation[14]:

$$E_{1/2} = 0.32\sigma^* + 0.12\,E_s - 2.16$$

It follows from this equation that the steric hindrance to electron transfer is considerably smaller than that resulting from an S_N2 reaction of RCH_2Br with such nucleophiles as OH^- or SCN^- (the coefficient of E_S in the above equation is unity). The steric hindrance in the

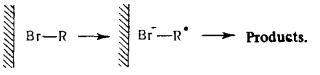
† The first wave exhibits a maximum whose nature is obscure. A similar maximum is always found in the reduction of mercury halides in anhydrous dimethylformamide.

cathodic reduction of these bromides is about the same as in the hydrolysis of esters, when the attacking nucleophile approaches the carbonyl carbon in a direction perpendicular to the C=O bond. It has been concluded[13] from these considerations that, in the cathodic reduction of alkyl bromides, the C–Br bond is oriented parallel to the electrode surface, and "perpendicular attack" takes place on the antibonding σ^*-orbital of the molecule:



Such a mechanism involves the intermediate formation of an unstable radical-anion $RBr^{\bullet}$, which breaks down rapidly into the radical $R^{\bullet}$ and the anion Br^-. Transfer of the second electron to $R^{\bullet}$ occurs rapidly, and does not affect the half-wave potential.

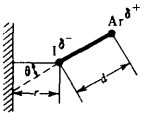
Sease et al.[15] consider that, in the reduction of bromides, the bromine atom is located at the surface of the mercury electrode, and the electron passes from the cathode to the carbon across the bridge formed by the bromine atom:



This hypothesis is based on the observation of reduction waves for compounds containing the bromine atom "in the bridgehead", e.g. 1-bromonorbornane, 1-bromobicyclo[2, 2, 2]octane, and bromotriptycene. If electrons had passed directly to the carbon atom, these compounds would not, in the opinion of the authors, have been reduced, owing to the considerable steric hindrance.

At the present time "perpendicular attack" and attack at the halogen atom are the most widely accepted views.

As the carbon–iodine bond in nuclear-substituted iodobenzenes becomes more ionic, the half-wave potential becomes more negative (the ionicity is determined from the nuclear quadrupole resonance spectra)[16,17]. It is impossible to explain this fact if the electron is assumed to pass to the carbon atom. Caldwell and Hacobian therefore supposed[17] that electron transfer occurs via the iodine atom. A somewhat modified spatial model of the reaction, as compared with that proposed by the authors, is given below:



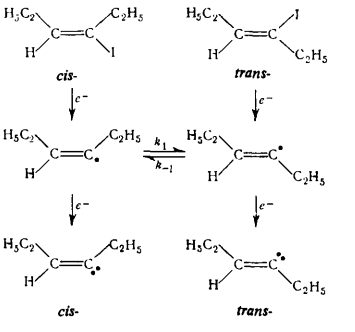
The ArI molecule is inclined at an angle $\frac{1}{2}\pi - \theta$ to the electrode surface, with the iodine atom closer than the carbon atom thereto. In passing to the iodine atom the electron traverses a distance r at an angle θ to the vector of the Ar–I bond. Accepting this orientation of the aryl iodide and putting $\cos\theta = 1$, these authors calculated the distance r between the iodine atom and the electrode surface from the slope of the linear plot of the ionic character of the bond against the half-wave potential. If the positive pole of the dipole is located on the carbon atom combined with the iodine, we have $\alpha = 2$ Å and the calculated value of $r = 1.2$ Å; if, however, the positive pole is located at the centre of the benzene ring ($d = 3.39$ Å), then $r = 1.4$ Å. The mean value of $r = 1.3$ Å agrees well with the van der Waals radius of iodine (1.33 Å). This was regarded as evidence, firstly that the iodobenzene molecule is perpendicular to the electrode surface during reduction, and secondly that the iodine atom is in close contact with the mercury surface[17]. However, the analogous calculation based on Lambert's model, in which the molecule of the halogeno-derivative is parallel to the electrode surface ($\cos\theta = 0$), gives $r = 1.05$ and 1.25 Å when $d = 2$ and 3.39 Å: i.e. the results are close to the values calculated by Caldwell and Hacobian and comparable with the half-thickness of the aryl iodide molecule.

Whatever the orientation of iodobenzene relative to the electrode surface, it follows from these calculations that reduction takes place with the molecule in close contact with the electrode, and electron transfer is effected at a distance less than 1.5 Å. It must be noted that the disposition of the transition state at the surface may depend on the potential of the electrode[1], but this question will not be examined here.

III. MONOHALOGENO- AND *gem*-DIHALOGENO-DERIVATIVES

As has already been remarked, a change in configuration of the group R during the cathodic reduction of halogeno-derivatives may occur either at the stage of formation of the radical $R^{\bullet}$ or at the stage of formation of the carbanion. The possibility of isomerisation of the radical formed as a result of transfer of the first electron has been well illustrated by the work of Fry and Mitnich[18]. The electrolysis of *cis*- and *trans*-3-iodohex-3-enes in dimethylformamide with tetra-n-butylammonium bromide as supporting electrolyte yields a mixture of *cis*- and *trans*-hex-3-enes, in which the *trans*-isomer always predominates (70–94%) independently of the configuration of the initial iodide. The course of the reaction can be represented by Scheme 1.

Scheme 1



In this case *cis*–*trans*-isomerisation can take place only at the stage of formation of the radical, since the vinyl carbanions formed by transfer of the second electron, unlike the corresponding radicals, are configurationally stable owing to the disadvantageous character of the allene structure. The *trans*-radical is thermodynamically more stable (i.e. $k_1 \gg k_{-1}$), and therefore the *trans*-hydrocarbon predominates in the reaction products.

The possibility of a change in configuration at the stage of radical formation is one factor leading to the usually low optical purity of hydrocarbons obtained by the electrolysis of optically active halides (see below).

If the rate of inversion of the radical exceeds the rate of transfer of the second electron, and the radical is able freely to change its orientation relative to the electrode surface, the hydrocarbon formed by reduction of an

optically active halide will be a racemate. If, however, even a proportion of the radicals form a surface compound with the mercury, electron transfer between the electrode and the radical will lead to formation of an optically active product, whose configuration will be determined by the disposition of the transition state on the electrode surface.

It is easy to understand that, in the reduction of saturated halogeno-derivatives, the stereochemistry of transfer of first and second electrons should be the same: otherwise it would be necessary to suppose that, for some unknown reason, the molecule rotates through 180° about an axis parallel to the electrode surface in the interval of time between these two processes ‡, or that the electron moves along a trajectory skirting the molecule. In the subsequent discussion of the stereochemistry, therefore, we shall not divide the transfer of the two electrons into two one-electron stages.

If interaction is assumed to occur between the halogen atom and the surface of the mercury electrode, the initial configuration of the carbanion formed by two-electron reduction of the molecule RX should coincide with the configuration of the initial halogeno-derivative. If, however, the transfer of electrons occurs on the side opposite to the liberated halogen atom, inversion of configuration should be observed. Henceforward we shall term these two cases "attack on halogen" and "attack on carbon" (the former corresponds to the "parallel" or "perpendicular" arrangement of the $R^{\delta+}-X^{\delta-}$ dipole considered above).

A general scheme of the reaction for cases of attack on halogen and on carbon (Fig. 2) shows the following stages—(1) actual transfer of electrons, (2) diffusion of initially formed carbanion from electrode surface into solution, (3) inversion of carbanion in solution, (4) and (5) protonation in solution of uninverted and inverted carbanions respectively, (6) transition of carbanion from sp^3 to sp^2 configuration as a consequence of conjugation with the substituent *d* (e.g. NO_2, COR, CN, etc.), (7) diffusion into solution of carbanion after having assumed a planar configuration, and its subsequent protonation, and (8) protonation of planar carbanion which has been unable to lose its bond with the electrode. It can be assumed from Fig. 2 that the stereochemistry of the cationic reduction of the carbon–halogen bond will depend on the stereochemical direction of five different stages in the process.

Table 1 shows the changes in configuration of the hydrocarbon formed by protonation at different stages in the conversion of the carbanions, compared with the configuration of the initial halogeno-derivative. The overall stereochemical result of the electrode reaction is seen to depend on the relative rates of the different stages: i.e. it is closely connected with the chemical structure of the initial halogeno-derivative and the resulting carbanion. In general it is fairly difficult to predict which stage will determine the stereochemistry to a greater extent, and which to a smaller extent, so that it is difficult to distinguish "attack on halogen" from "attack on carbon". To settle this question it is necessary to choose an organic halogeno-derivative which will give a configurationally stable carbanion on reduction, i.e. a carbanion which will not contain substituents *d* capable of stabilising it by conjugation and localisation of a negative charge on a heteroatom, and which would possess a low rate of inversion.

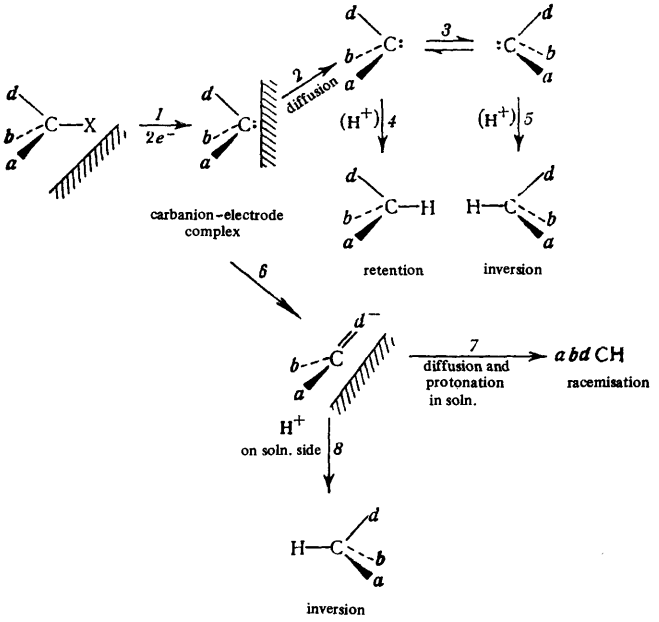


Figure 2. Events occurring during lifetime of carbanion formed by cathodic reduction of an optically active halogeno-derivative. The scheme shows the case in which electron transfer occurs with retention of configuration.

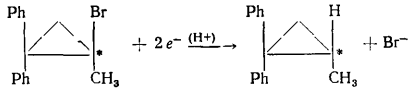
Table 1.

Stage of reaction	*1*	*4*	*3.5*	*6.7*	*6.8*
Attack "on halogen"	retention	retention	inversion	racemisation	inversion
Attack "on carbon"	inversion	inversion	retention	racemisation	retention

These requirements are satisfied by halogenated vinyl and cyclopropyl derivatives. Cyclopropyl anions are inverted at a very low rate [19]—less than twice a second—so that the stereochemical contribution of reactions (3) and (5)—and, in the absence of substituents capable of conjugation, also reactions (6–8) and (6–7)—is not so large. Thus it may be expected that the stereochemistry of the cathodic reduction of cyclopropyl halides will be determined in considerable measure by the stages of actual transfer of electrons (1) and of diffusion of the carbanion into the solution (2). Hence it is not surprising that almost all work on the stereochemistry of the cathodic reduction of halogeno-derivatives has been done on derivatives of cyclopropane. Study of the stereochemistry of these reactions shows that electron transfer occurs with retention of configuration, i.e. on the side of the halogen atom.

‡ This does not apply to the *cis*- and *trans*-iodohexenes discussed above, which by analogy with other π-systems probably have a horizontal orientation relative to the electrode surface. If a stage of isomerisation of the radical is involved, therefore, the stereochemistry of transfer of first and second electrons may be different.

Walborsky and his coworkers[20] electrolysed (+)-(*S*)-1-bromo-1-methyl-2,2-diphenylcyclopropane in acetonitrile at a mercury cathode at a potential of −2.7 V (s.c.e.). This gave a 93% yield of the corresponding hydrocarbon, which had the configuration of the original bromide (25% optical purity):



The current–time curve obtained at a stationary macroelectrode had an unusual form. A mercury-containing product appeared in the solution at the start of electrolysis, and the mean consumption of electrons per R–Br molecule was < 2. Results obtained by cyclic volt–amperometry suggested the mechanism of reduction

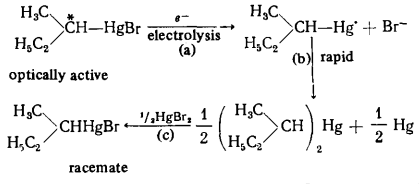
$$R{-}Br + e^- \rightarrow (R{-}Br)^{\cdot-} \qquad RHg_n^{\cdot} + e^- \rightarrow R^- + Hg_n$$

$$(R{-}Br)^{\cdot-} \rightarrow R^{\cdot} + Br^- \qquad RHg_n^{\cdot} + RHg_n^{\cdot} \rightarrow RHg_nR + RHgR + Hg_{n-1}$$

$$R^{\cdot} + e^- \rightarrow R^- \qquad R_2Hg + e^- \rightarrow R^- + RHg^{\cdot} \xrightarrow{Hg} RHg_n^{\cdot}$$

$$R^{\cdot} + Hg_{\perp} \rightarrow RHg_n^{\cdot} \quad R^- + H^+ \rightarrow RH$$

The retention of configuration in this case might have been explained by a double inversion of configuration at the stages of electrolysis of RBr and formation of R_2Hg[5]. According to Dessy et al.[21], however, optically active s-butylmercuric bromide is completely racemised during electrolysis. This is proved by the cycle of reactions



Electrolysis of optically active s-butylmercury bromide produces an organomercury radical, which then dimerises rapidly to di-s-butylmercury. The action of mercury(II) bromide on this last compound yields optically inactive s-butylmercury bromide. It has been duly proved that stage (*c*) occurs with retention of configuration[22], and therefore racemisation should take place at either stage (*a*) or stage (*b*). Disproportionation of RHg· radicals (reaction *b*) involves rupture of only one C–Hg bond: i.e. if stage (*a*) leads to the retention of configuration, the optical activity of RHgBr obtained from R_2Hg should be partly retained. Hence it may be concluded that the RHg· radicals are optically inactive: i.e. racemisation occurs at the stage of formation of RHg· from RHgBr.

This conclusion is consistent also with the fact that the reduction at a mercury electrode of phenylmercuric bromide containing the radioactive isotope ^{203}Hg is accompanied by rapid isotopic exchange between the organomercury compound and the metallic mercury of the electrode, whereas on open circuit such exchange is almost zero[21]. This implies that organomercury radicals are involved in the isotopic exchange:

$$Ph{-}{}^{203}Hg^{\cdot} + Hg \underset{}{\overset{rapid}{\rightleftharpoons}} PhHg^{\cdot} + {}^{203}Hg$$

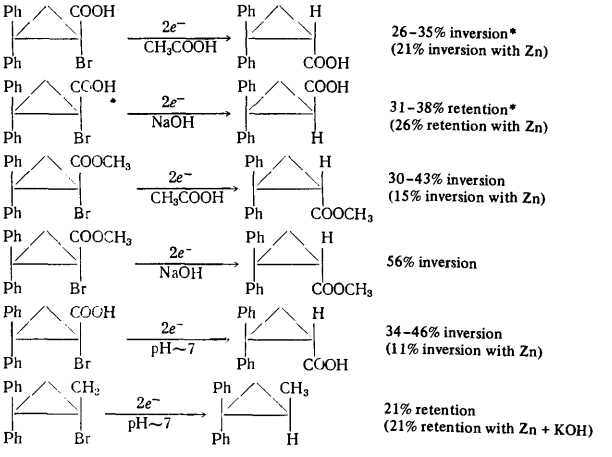
It is natural to expect that such exchange will be accompanied by racemisation, since the reaction involves fission of the carbon–mercury bond§.

§ Thus data on the stereochemistry of the reduction of organomercury compounds cannot be used in discussing the question of the distance between the depolariser and the electrode.

It is clear that the corresponding organomercury compound is not an intermediate product in the reduction of 1-bromo-1-methyl-2,2-diphenylcyclopropane. Besides the reason mentioned at the beginning of this Section, the incomplete retention of the configuration can be explained also by the partial occurrence of the reaction via the organomercury compound and partial inversion of the carbanion in solution (stages (2) and (3) in Fig. 2).

Annino et al.[23] have also investigated the cathodic reduction of optically active 1-bromo-1-methyl-2,2-diphenylcyclopropane in alcoholic medium at potentials of ~2.3 V (s.c.e.). The product was a hydrocarbon of 21% optical purity (retention of configuration), which agrees with Walborsky's results[20]. An investigation was made also of the stereochemistry of the reduction at a mercury electrode of optically active 1-bromo-2,2-diphenylcyclopropanecarboxylic acid and its methyl ester at various solution pH values produced by the addition of acetic acid or of sodium hydroxide to the alcoholic solutions. The results are shown in Scheme 2. The stereochemistry of the cathodic reduction of these bromo-derivatives corresponds qualitatively to that of their reduction with metallic zinc (these results are given in parentheses in Scheme 2).

Scheme 2

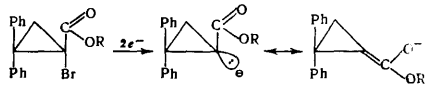


* The expression "30% inversion" means that the result of reduction is a hydrocarbon whose absolute configuration is opposite to that of the initial bromide, while the yield of this hydrocarbon is 30% of the initial bromide of 100% optical purity (the remaining 70% of the total quantity of cathodic reduction product comprises a racemate). The "percentage retention of configuration" is to be interpreted analogously.

The results are explained on the basis of two fundamental assumptions: (1) electron transfer to the cyclopropyl bromide molecule occurs on the side containing the bromine atom, with formation of a carbanion having the configuration of the original bromide; and (2) the general stereochemistry of the process is determined by the stereoselective reaction of the carbanion, either free or shielded by the electrode, with a proton donor.

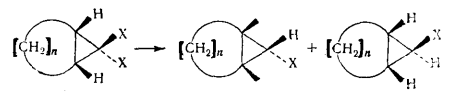
In the case of the brominated cyclopropanecarboxylic acids the carbanion formed by reduction is able to assume

a planar configuration as a consequence of conjugation with the carbonyl group:



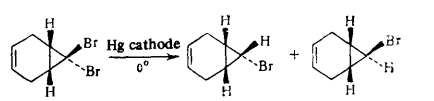
In contrast to 1-methyl-2,2-diphenylcyclopropyl bromide, therefore, such compounds are reduced with retention of configuration. In this case the stereochemistry of the reaction is probably determined by stages (6)–(8) (Fig. 2). The fact that in alkaline medium 1-bromo-2,2-diphenylcyclopropanecarboxylic acid is reduced with retention of configuration (Scheme 2) is probably due to the considerably diminished stabilisation of the planar anion owing to ionisation of the carboxy-group.

The cathodic reduction of *gem*-dihalogenocyclopropanes is highly stereoselective. Fry and Moore[24] have examined the composition of the products of the electrolysis of 1,1-dihalogeno-2,3-tetra(and hexa)methylenecyclopropanes in various solvents. The reaction results in detachment of one halogen atom with formation of a monohalogenocyclopropane, the main product in all solvents being the *cis*-isomer:



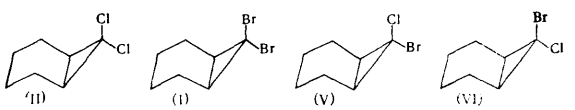
I: $n = 4$, X = Br
II: $n = 4$, X = Cl
III: $n = 6$, X = Br

cis- (*endo*-) *trans*-(*exo*-)



(IV) *cis*- *trans*-

Similar results have been obtained by Annino and his coworkers[25], who investigated the compounds



(II) (I) (V) (VI)

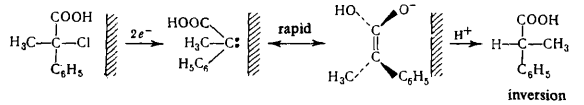
In compounds (V) and (VI), which contain both chlorine and bromine, the bromine is reduced. Table 2 gives the proportions of *cis*- and *trans*-monohalogeno-derivatives (the *endo/exo* ratios) determined by gas–liquid chromatographic analysis of the products of the electrolysis. The ratio of the isomers in the reaction product depends not only on the nature of the solvent but also on the inert electrolyte.

Three conclusions can be drawn from the above results: (1) *cis*-monohalogeno-compounds are the main products of the electrolysis of dibromo- and dichloro-derivatives; (2) the content of the *cis*-isomer increases with increase in the concentration of water in the solution; and (3) the stereospecificity of the reaction is greater with chloro- than with bromo-derivatives. The results can be explained by two alternative schemes: firstly, of two identical halogen atoms, that one is reduced which is located in the *cis*-position to the hydrogen atoms adjacent to the bond between the rings, in which case electron transfer occurs with retention of the configuration; or secondly the *trans*-halogen is reduced with inversion of the configuration.

If "attack on halogen" is supposed to occur (see above), steric hindrance on formation of the transition state is far greater for a halogen in the *trans*-position to the hydrogen atoms of the bridging bond. This is supported by the fact that the reduction of bromine in the two isomeric 7-bromo-7-chlorobicyclo[4,1,0]heptane occurs with greater difficulty in (VI) than in the isomer (V), in which the spatial position of the bromine is more favourable for approaching the electrode surface.

The stereospecificity of the cathodic reduction of different halogens (Cl > Br) is analogous to that observed in the preparation of Grignard reagents from cyclopropyl halides. This occurs with retention of configuration, the loss of optical activity falling in the sequence I > Br > Cl[26]. The mechanism of the reaction RX + Mg → RMgX is probably similar to that of the cathodic reduction of the halides[27]. Preferential formation of *endo*-isomers is observed also in the reduction of compounds (I), (II), and (V) with zinc or lithium amalgam in alcohol[25].

Optically active α-chlorohydratropic acid is reduced with inversion of configuration[28]. This result is explained by "attack on carbon" and accompanying inversion. However, as with the halogenated cyclopropanecarboxylic acids (Table 2), a better explanation is "attack on halogen" and rapid transition of the carbanion into a planar configuration. Owing to the shielding effect of the electrode, subsequent protonation occurs predominantly on the solution side:



inversion

Table 2. Stereochemistry of the electrolysis of *gem*-dihalogenocyclopropanes at a controlled potential.

Compound	Solvent-electrolyte*	Ratio of isomeric products (*endo/exo*)
I	DMF-LiCl	1.6
	96% DMF—4% H_2O—LiCl	3.0
	CH_3OH—LiCl	1.9
	95% CH_3OH—5% H_2O—LiCl	2.7
	95% CH_3OH—5% HCl—LiCl	3.5
	90% CH_3OH—10% H_2O—LiCl	5.3
	CH_3COOH—TEAB	4.0
II	DMF—LiCl	4.3
	96% DMF—4% H_2O—LiCl	5.3
	CH_3OH—LiCl	19.0
	95% CH_3OH—5% HCl—LiCl	only *endo*
	33% HMPTA—67% C_2H_5OH	only *endo*
III	CH_3OH—LiCl	only *endo*
	95% CH_3OH—5% HCl—LiCl	only *endo*
IV	CH_3OH—LiCl-	2.7
	90% CH_3OH—10% H_2O—LiCl	10.0
V	C_2H_5OH—TEAB	3.6
	C_2H_5OH—LiCl	2.6
VI	C_2H_5OH—LiCl	0.38
Mixture of V + VI (1:1)	C_2H_5OH—LiCl	1

* DMF = dimethylformamide; HMPTA = hexamethylphosphorotriamide; TEAB = tetraethylammonium bromide.

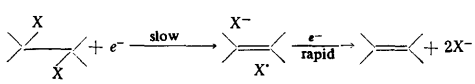
Reduction by zinc in acetic acid proceeds similarly. Ott and Kramer[29] reported that α-chlorohydratropic acid is reduced by this system with inversion of configuration, but by hydrogen–palladium with its retention. According to Brewster[30] inversion of configuration is a result of direct interaction between zinc and the chlorine atom: a carbanion is formed which is then rapidly protonated, before it is able to diffuse into the solution, i.e. to free itself from the metal surface.

Thus it may be concluded that, in the preparative electrolysis of optically active halogeno-derivatives, electron transfer to the molecule RX occurs on the side of the halogen atom in close contact with the electrode surface; this leads to the formation of a carbanion having the same configuration as the initial bromide. However, subsequent events occurring in the lifetime of the carbanion (inversion, resonance stabilisation, diffusion into the solution) may influence considerably the overall stereochemical result of the reaction. Depending on the properties of the organic halogeno-derivative, therefore, either retention, inversion, or complete racemisation of the configuration may be observed.

IV. VICINAL DIHALOGENO-DERIVATIVES

Most cases of the cathodic reduction of vicinal dihalogeno-derivatives involve the simultaneous detachment of two halide anions with the formation of a multiple bond. Thus the electrolysis of 1,2-dibromoethane yields ethylene and ethane[31]. This reaction recalls the formation of alkenes, which occurs when vicinal dibromides are treated with zinc or magnesium. The mechanism of the reduction of such compounds has already been considered in a review[5]. Here we shall discuss briefly only the stereochemical aspects of this reaction.

cis-1,2-Dibromocyclohexane is reduced at a potential of −1.85 V (s.c.e.) and the *trans*-isomer far more easily (−1.0 V)[32]. *meso*-2,3-Dibromosuccinic acid is more easily reduced than is the (±)-isomer[33], and this applies also to *meso*-2,3-dibromobutane-1,4-diol[34]. The greater ease of reduction of *meso*-dihalides implies that *trans*-elimination occurs preferentially. In the case of rigid bicyclic systems the *cis*-dibromides are more easily reduced, since a *trans*-coplanar configuration cannot exist[35,36]. Detachment of the two halogen atoms probably occurs simultaneously:



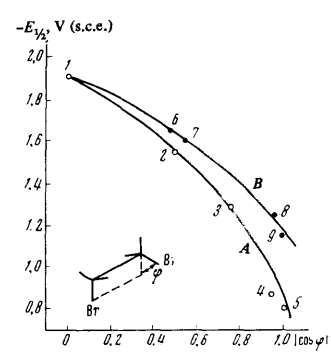
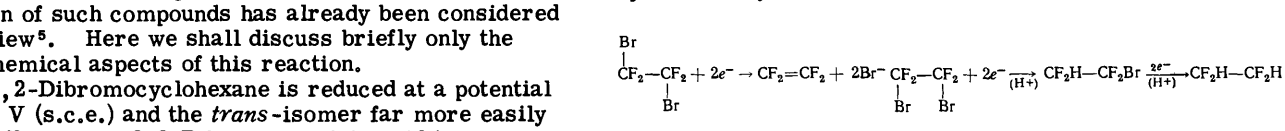


Figure 3. Dependence of half-wave potential of vicinal dibromides on dihedral angle between C−Br bonds:
A) compounds having an *anti*-planar configuration ($120° \leqslant \varphi \leqslant 180°$); B) compounds having a *syn*-planar configuration ($0° \leqslant \varphi \leqslant 60°$). It is clear that an *anti*-planar configuration is more favourable.

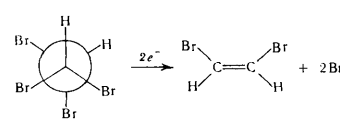
It can be shown that both halogen atoms are involved in formation of the transition state. Zavada et al.[36] determined half-wave potentials for a large number of vicinal dibromides and monobromides. In the series of dibromides $E_{\frac{1}{2}}$ varies from −0.82 to −1.67 V, but in the series of monobromides from −1.90 to −2.16 V (s.c.e.). The compounds were selected so that the steric hindrance was about the same in the two series, i.e. so that it made a relatively small contribution to variation in the reduction potentials. The main reason for the marked variation in the half-wave potentials in the vicinal dibromides is the variation in the dihedral angle φ between the planes formed by each bromine atom with the carbon–carbon bond. The graph in Fig. 3 shows that molecules having an *anti*- or *syn*-planar arrangement of the bromine atoms (φ = 180° or 0°) are reduced at more positive potentials than are molecules in which the angle φ lies between 60° and 120°.

Other evidence of the simultaneous detachment of two bromine atoms has been obtained by Feoktistov and Gol'din[37] in a study of the cathodic reduction of 1,2-dibromotetrafluoroethane. The product of reduction of the *anti*-isomer is tetrafluoroethylene, whereas the *syn*-isomer yields tetrafluoroethane¶:



Not only halogens but also other electronegative groups, e.g. hydroxyl and acetoxyl, may be split off together with a bromine atom[33]. In these cases reduction is also facilitated when the two groups are located in the same plane.

The electrolysis of tetrabromoethane yields a mixture of *cis*- and *trans*-dibromoethylene in the proportions 6:1[39,40]. These results show that *trans*-elimination predominates, since in polar solvents (50% aqueous ethanol was used in this example) tetrabromoethane exists predominantly as the staggered conformation:



cis- and *trans*-Dibromoethylenes are formed in the ratio 6:1, differing considerably from the proportions in the reduction of tetrabromoethane by zinc or by tin(II) chloride (1.2–2:1). The probable reason is that, during electrolysis within the potentials of the limiting diffusion current, i.e. with diffusion control of the reaction, the staggered conformation is unable to pass into the more reactive transoid conformation[40], whereas with kinetic control (dehalogenation by zinc) such conversion is possible.

¶ However, successive replacement of chlorine by hydrogen has been observed[38] in the electrolysis both of diethyl dichloromaleate and of diethyl dichlorofumarate. Reduction of the corresponding dibromo- and di-iodo-esters proceeds "normally": i.e. acetylenedicarboxylic ester is formed[38].

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Gas Chromatography at High Eluent Pressures

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The influence of pressure on the efficiency of a chromatographic column and on the selectivity of the stationary phase has been investigated. The role of pressure gradients along the column has been demonstrated. It is shown that the efficiency can be drastically increased by turbulence in the carrier gas stream. A special study is made of the use of eluents under supercritical conditions, which permits involatile compounds with a molecular weight up to 4000000 to migrate along the column.
The use of chromatography in studies of non-ideality in the gas phase is discussed. In particular, we have considered the determination of the second mixed virial coefficients in the equation of state for the gas, and the non-ideality corrections needed to determine the activity coefficients of solutes. 115 references.

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I. INTRODUCTION

The most significant advances in analytical gas chromatography since 1958 are the use of capillary columns[1] and the development of highly sensitive detectors of the ionisation type[2,3]. These developments have transformed gas chromatography into a universal method of analysis of complex mixtures of organic and inorganic compounds, ranging from permanent gases to substances having vapour pressures of the order of thousandths of a mmHg at the temperature of the experiment[4]. The introduction of detectors sensitive to $10^{-7}-10^{-8}$ mg has allowed the size of the analytical sample to be made as small as $10^{-2}-10^{-4}$ mg.[5] The efficiency of capillary columns, measured in hundreds of thousands of theoretical plates, has now become commonplace[6,7]: conformational isomers[8] can often be separated, and isotope effects[9] can be studied. The time needed for a complete analysis has been shortened to the point that light hydrocarbon mixtures can now be separated in times of the order of a second[10,11].

Because these applications of gas chromatography fulfilled actual practical needs, their realisation was very rapid. It soon became apparent that analytical gas chromatography needed to be developed further before it could be applied to substances of high molecular weight and to relatively unstable compounds (without resorting to reaction chromatography).

Evidently, the scope of chromatographic separation can be extended towards high-molecular-weight compounds by decreasing the distribution coefficients of the sorbates. The major development in gas chromatography in recent years have been in this direction. The main stages in this development have been the introduction of gas–liquid chromatography, the use of carriers very lightly impregnated with the stationary phase, the adoption of capillary chromatography, the development of temperature programming, and the use of weak adsorbents. Actually, the partial Henry coefficient (the ratio of the capacities of the stationary and the mobile phase),

$$\Gamma^{\mathrm{I}} = \frac{t_R}{t_0} - 1 = \frac{c_s \varkappa_{\mathrm{I}}}{c_g \varkappa} \qquad (1)$$

is related to the retention time t_R of the sorbate. (t_0 is the retention time of the non-adsorbed material.) The Henry coefficient is determined by the concentration of the sorbate in the gas (c_g) and the sorption (c_S) phase, and by the ratio of the volumes κ and κ^{I} occupied by these phases in the column.

Thus, the use of gas–liquid chromatography, of weak adsorbents, and also of temperature programming leads to smaller values of c_S, whereas the use of columns with a small percentage of impregnant (capillary columns) decreases κ^{I} and increases κ.

The distribution coefficients can be further decreased (to the point where they are practically independent of the vapour pressure of the sorbate) by increasing the solubility of the sorbates in the mobile phase. To this end, the eluents are applied in the form of gases at high pressure, or liquids.

The earliest report of the successful application of gas chromatography at pressures above 100 atm was due to Klesper and coworkers[12], who were able to separate mixtures of porphyrins. Subsequent work by Giddings and coworkers[13–15], and also by Sie and coworkers[16–18], showed that polynuclear aromatics, polymers with molecular weights in excess of 400 000, and many other high-molecular-weight compounds can be separated by gas chromatography.

Giddings has pointed out[15] that gas chromatography at high pressures has three main advantages over liquid chromatography: 1) the distribution coefficient of the sorbates between the stationary and the mobile phase can be controlled over wide limits by changing the pressure; 2) the analysis is faster because the mobile phase is less viscous and the diffusion coefficients of the sorbates are higher; 3) detectors with much higher sensitivity can be used.

Increase in pressure within the column affects the analysis time, the selectivity of the column, and the efficiency of the process, and therefore pressure is one of the most important parameters of a fast column.

The "speed coefficient" is defined[19,20] as

$$\lambda = \frac{n_p \cdot K^2}{t} \sim k \left(\frac{\Gamma'}{\Gamma'+1}\right)^2 \cdot \frac{n}{t} \qquad (2)$$

where n_p is the number of peaks in the chromatogram, K is the degree of resolution of the least resolved pair, t is

the time of analysis, k_S is the selectivity coefficient for the sorbate, n is the number of theoretical plates, $\Gamma' = \Gamma\frac{K'}{K}$ is the partial Henry coefficient (mean value for the components of the least resolved pair), Γ is the true Henry coefficient (ratio of concentrations of the sorbate, in g ml^{-1}, in the stationary and the mobile phase). Thus, since k_S is determined by the Henry coefficient for the components of the least resolved pair, and t is determined by the Henry coefficient of the most strongly held component of the mixture, all the quantities in the right-hand side of Eqn. (2) are a function of the nature of the eluent and of its pressure.

These relationships are discussed in the present review together with the possible practical applications of gas chromatography at high pressures.

In addition to its advantages in the field of analytical chromatography, the use of high pressures offers new scope in non-analytical applications of gas chromatography. These include methods of studying non-ideality in gases, the determination of the constants for phase equilibria in multicomponent systems, etc., which are also discussed in the following Sections.

II. INFLUENCE OF PRESSURE ON THE EFFICIENCY OF A CHROMATOGRAPHIC COLUMN

The effect of pressure on the efficiency of a chromatographic column has been discussed by many workers[21-34] in the absence of non-ideality effects, i.e. for pressures below 5 atm. Assuming pressure-independence of the dynamic viscosity of the carrier gas and of the permeability of the column, and also assuming laminar flow conditions, the square of the width of the band for a particular component,

$$\sigma_{st}^2 = \int_0^L H\left(\frac{P}{P_0}\right)^2 dx \qquad (3)$$

(where H is the height equivalent to a theoretical plate at the cross-section of the column where the pressure is P, and P_0 is the pressure at the column outlet) is given by

$$\sigma_{st}^2 = L\left(A + \frac{B}{\bar{P}\bar{\alpha}} + E\bar{P}\bar{\alpha} + C_2\bar{P}^{0.5}\bar{\alpha}^{0.5}\right)\frac{1}{\chi^2} + LC_1\bar{\alpha}\cdot\frac{1}{j^2} \qquad (4)$$

Here σ_{st} is the mean standard deviation (the half-width of the peak at a height $1/\sqrt{e}$ of the maximum height) on the layer of sorbent when elution occurs, L is the length of the column, A is the turbulent diffusion term in the equation for the height equivalent to a theoretical plate, B is the molecular diffusion term, E accounts for contributions from the wall effect, from outer diffusion of weakly sorbed materials, and from dynamic diffusion, C_2 is the mass transfer term for outer diffusion (as defined by Zhukhovitskii and Turkel'taub[35]), C_1 is the mass transfer term for inner diffusion, $\bar{P}$ is the mean pressure in the column, $\bar{\alpha}$ is the mean linear velocity of the carrier gas, the parameter χ is given by

$$\chi = \sqrt{\frac{2}{(P_1/P_0)^2 + 1}},\quad j = \frac{3}{2}\frac{(P_1/P_0)^2 - 1}{(P_1/P_0)^3 - 1},$$

P_1 is the pressure at the column inlet, and P_0 is the pressure at the column outlet.

At pressures of hundreds of atmospheres, when the deviations from ideality of the gas are large and neither the viscosity, nor the product $P\alpha$, nor the distribution coefficient of the sorbate are constant along the column, integration of Eqn. (3) leads to very complicated expressions[36].

The factors χ and j have very similar values, so that the ratio j^2/χ^2 does not exceed 9/8. Hence we may conclude[33] that the efficiency of the column is practically independent of the pressure drop and is determined only by the mean pressure in the column. Thus, if we assume that the spreading of the peak is limited by inner diffusion, the number of theoretical plates deduced from the experimental values of retention volume (V_R) and peak width (ω), both in ml, is

$$n = \frac{V_R^2}{\omega^2} = \frac{V_R^{02}}{j^2}\cdot\frac{j^2}{\omega^{02}} = n^0 \qquad (5)$$

Here $V_R^0 = V_R \cdot j$ is the corrected retention volume, $\omega^0 = \omega \cdot j$ is the corrected peak width, n^0 is the corrected number of theoretical plates corresponding to a mean pressure $\bar{P}$ in the absence of significant pressure gradients along the column.

If the term C_1 can be neglected, we may write[37]

$$n = \frac{V_R^{02}}{j^2}\cdot\frac{\chi^2}{\omega^{02}} = n^0\cdot\frac{\chi^2}{j^2} \qquad (6)$$

Thus, the decrease in the number of theoretical plates at high pressure gradients is not very large (and cannot exceed 11.1%†).

It follows that the height equivalent to a theoretical plate is

$$H = \frac{L}{n} = \frac{j^2}{\chi^2}\left(A + \frac{B}{\bar{P}\bar{\alpha}} + E\bar{P}\bar{\alpha} + C_2\bar{P}^{0.5}\bar{\alpha}^{0.5}\right) + C_1\bar{\alpha} \approx H^0 \qquad (7)$$

where H^0 corresponds to a mean pressure $\bar{P}$ and small pressure gradients.

Introducing the symbol $r = \bar{P}\bar{\alpha}$, the minimum value of H^0 is

$$H^0 = A + \frac{B}{r} + Er + C_2 r^{0.5} + C_1\frac{r}{\bar{P}} \qquad (8)$$

If, for simplicity, we ignore the term in C_2,

$$H^0_{min} = A + 2\sqrt{B\left(\frac{C_1}{\bar{P}} + E\right)}, \qquad (9)$$

and the corresponding value of r is

$$r_{opt} = \sqrt{\frac{B}{\frac{C_1}{\bar{P}} + E}} \qquad (10)$$

The effect of pressure on the analysis time can be characterised by the "speed coefficient". If, under the particular experimental conditions, the main contribution to the diffuseness of the bands comes from the terms E and C, it follows that[33]

$$\lambda \sim \frac{n}{t} \sim \frac{1}{E\bar{P} + C_1} \qquad (11)$$

The following conclusions may be made from the above considerations.

1. The efficiency of the column is degraded by operating at higher pressures if the optimum value of the carrier-gas velocity is used for the separation.

† It should be noted that these conclusions are independent of the chosen model for the spreading process. Identical results have been obtained using Giddings' "conjugated" theory[38].

2. The optimum carrier velocity decreases as the pressure in the column increases. Thus, as Fig. 1 shows, the left-hand branch of the hyperbola is shifted towards very low velocities when the pressure is increased.

3. The speed coefficient increases, tending asymptotically to a limit proportional to $1/C_1$, as the pressure decreases. Thus, it is desirable to use a moderate vacuum[33] when a short analysis time is required.

4. For a constant average velocity in the column, the relationship between H and the mean value of $\bar{P}$ is a hyperbola with a slanting, curved branch[28] [see Eqn. (7)].

5. The plot of H against α_0 (where α_0 is the linear velocity of the gas at the outlet of the column) is not a hyperbola. The right-hand side of the curve becomes steeper as the velocity increases[17,33] because of the decrease in the term C_1r/P [see Eqn. (8), with the assumption that $\bar{P}\bar{\alpha} = P_0\alpha_0$].

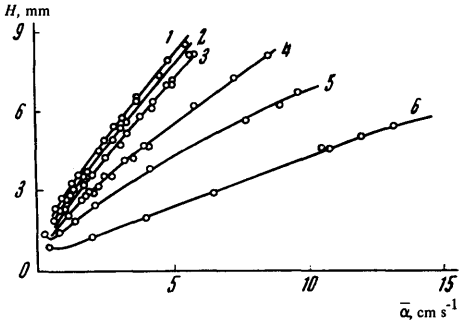

Figure 1. Effect of pressure on the dependence of the HETP on the mean velocity of the carrier gas. Sorbate: pentane; eluent: carbon dioxide. Temperature 40°.[17] Pressure: *1*) 50, *2*) 40, *3*) 30, *4*) 20, *5*) 10, *6*) 5 atm.

The effect of pressures of the order of tens or hundreds of atmospheres on the efficiency of the column is discussed by Giddings and coworkers[39-42]. Assuming that under these conditions the gas velocity is almost proportional to the inlet pressure P_1, Eqn. (7) takes the form

$$H \approx A + \frac{B}{P_1^2} + EP_1^2 + (C_1 + C_2)P_1 \qquad (12)$$

(where the symbols have the meaning already stated).

On the other hand, according to the "conjugated" theory of Giddings[39],

$$H \approx \frac{1}{\frac{1}{A} + \frac{1}{EP_1^2}} + \frac{B}{P_1^2} + C_1P_1 \qquad (13)$$

and, in our terminology, since $t = \frac{L}{\alpha}\Gamma_0$ where $\Gamma_0 = \Gamma\kappa_1 + \kappa$ and $n = L/H$,

$$\lambda \sim \frac{n}{t} \sim \frac{\alpha}{H\Gamma_0} \sim \frac{1}{\frac{H}{P_1}\Gamma_0} \qquad (14)$$

It follows from Eqns. (13) and (14) that the speed coefficient tends towards the limit $1/C_1\Gamma_0$ as the pressure increases (if we ignore the effect of pressure on the selectivity of the column).

Giddings has shown[43] that the minimum time to achieve an efficiency of n theoretical plates for an inlet pressure P_1 is

$$t = nC_1\Gamma_0 \cdot \frac{P_1^2}{P_1^2 - P_c^2}, \qquad (15)$$

where P_c is the "critical" pressure for the prescribed efficiency[44], whose numerical value is of the order of $4 \times 10^{-2}\sqrt{n}$ for conventional packed columns. If a separation criterion $K = 1$ is required, then

$$P_c \approx \frac{0.2}{K_c} \qquad (16)$$

For $P_1 \gg P_c$ and $t = nC_1\Gamma_0$, a very fast action becomes possible. Thus, Fig. 2 shows a chromatogram of petroleum gases obtained in under 1 min at $P_1 = 172.6$ atm.

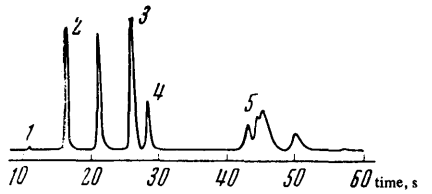

Figure 2. Separation of petroleum gas. Column length 1 m, internal diameter 0.47 mm. Sorbent: aluminium oxide. Pressure at column inlet 172.6 atm. Temperature 25°. *1*) air peak, *2*) propane, *3*) isobutane, *4*) n-butane, *5*) isobutene.

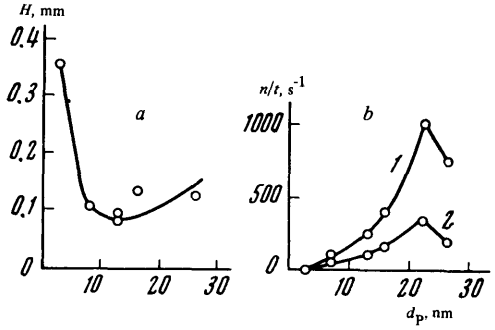

Figure 3. (*a*) Variation of HETP with average particle size of the filling (adsorbent: aluminium oxide)[40]. (*b*) Number of theoretical plates generated per second, *1*) for methane and *2*) for butane, against average particle size of the aluminium oxide[40].

In cases where the effect of non-equilibrium conditions can be almost completely eliminated, it becomes apparent that the efficiency is affected by the turbulent diffusion factor $A = 2\lambda_1 d_P$, where λ_1 is the tortuosity coefficient and d_P is the diameter of the sorbent particles. Fig. 3 shows plots of the height equivalent to a theoretical plate, and of the ratio n/t, against particle diameter for a column of 0.47 mm diameter.

Giddings finds that[43]

$$\frac{n^2}{t} = (10^6 \div 10^7)\Delta P, \qquad (17)$$

where ΔP is the pressure drop in the column.

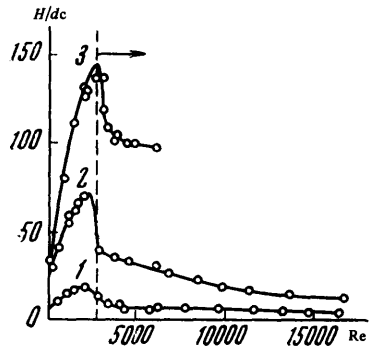

Figure 4. Reduced HETP against Reynolds number for: *1*) methane in nitrogen, *2*) pentane in nitrogen, and *3*) pentane in helium. Capillary column 21.3 m long. Temperature 0°.[45]

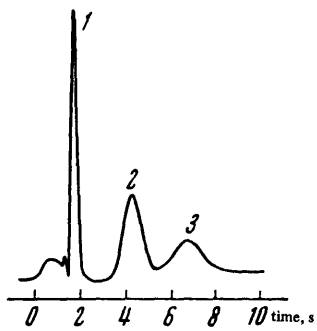

Figure 5. Chromatogram for the separation of light hydrocarbons in a stream of helium (turbulent regime, Re ≃ 7000). Temperature 74°. Pressure at column inlet 144 atm. *1*) propane, *2*) n-butane, *3*) n-pentane.[45]

All the considerations discussed above are based on the assumption of laminar gas flow, which is reasonable for normal gas velocities in a chromatographic column. Turbulent flow, which tends to equalise the velocities in a cross-section of the tube and to improve the mass transfer between the phases[45-52], produces a drop in the right-hand branch of the $H-\alpha$ curve at sufficiently high values of the Reynolds number ($\mathrm{Re} = \frac{d\alpha\rho}{\eta}$, where ρ and η are the density and the dynamic viscosity of the gas respectively, and d is the hydraulic diameter of the tube). Both the velocity and the density of the eluent increase with pressure: for example, for carbon dioxide the ratio ρ/η is 1000 s cm^{-2} at 80 atm (40°), as compared with 1 s cm^{-2} at 1 atm.[17]

Whereas the transition to the turbulent regime occurs at Re = 2130 in capillaries, in packed columns the turbulent regime is reached at Re values of the order of 1–100.[43]

Giddings and coworkers[45] achieved Reynolds number of the order of 16 000 at mean velocities in excess of 2000 cm s^{-1} and pressures up to 2000 atm, corresponding to almost sonic velocities at the column outlet. Fig. 4 shows plots of the efficiency (ratio of H to diameter) of a capillary column, coated with an adsorbent[53], against the Re number. It is evident that the efficiency increases sharply at the transition to the turbulent regime (the quantity H is smaller by a factor of 40 than the value expected from the conventional theory, which assumes laminar flow).

Giddings and coworkers have shown that at Re = 16 000 the speed coefficient is so high that the column generates 2500 theoretical plates per second for pentane (nitrogen carrier gas), and over 8000 theoretical plates for methane. Fig. 5 shows a chromatogram of light hydrocarbons, obtained at −74° and a column inlet pressure of 144 atm, corresponding to Re ≃ 7000.

Similar effects have been noted with packed columns[45].

III. INFLUENCE OF NON-IDEALITY IN THE GAS PHASE ON THE RETENTION OF SORBATES IN A CHROMATOGRAPHIC COLUMN

The influence of non-ideality of the carrier gas on the retention properties of sorbates was first recognised by Goldup and coworkers[54], who showed that the replacement of hydrogen by nitrogen as the carrier gas in long capillary columns operated with an inlet pressure of ~10 atm has a significant effect on the selectivity of the column towards hydrocarbon separation. The effect was ascribed[54,55] to the dependence of the coefficient Γ' upon the second virial coefficient in the equation of state of the gaseous mixture of sorbate and carrier gas. This dependence stems from the familiar expression[56]

$$\Gamma = \Gamma^0 e^{\beta P} \qquad (18)$$

where the coefficient Γ^0 corresponds to $P \to 0$, and β is a coefficient whose value depends on the non-ideality of the gas phase (see Section IV).

The present writers[57,58] have studied the chromatographic behaviour of hydrocarbons from wide petroleum fractions in capillary columns coated with octadec-1-ene and poly(ethylene glycol)-400 using inlet pressures up to 30 atm and helium, nitrogen, argon, and carbon dioxide as carrier gases.

Over that pressure range, an almost linear relationship was observed between the retention index of the sorbate and the mean column pressure, the slope $(\partial I/\partial P)_T$ being sensitive to the structure of the sorbate molecule and having different values for isoalkanes, alkenes, and aromatic hydrocarbons. This effect occasionally leads to an inversion of the elution order. In a poly(ethylene glycol) column, the retention index of alkylbenzenes changes by 30–40 units on raising the pressure to 30 atm, and this effect produces a large increase in selectivity for the separation of aromatic from aliphatic hydrocarbons.

Giddings' treatment[59] of the effect of non-ideality in the gas phase upon the retention characteristics is based on the expression

$$RT\left(\frac{\partial \ln \Gamma}{\partial P}\right)_T = -\delta V_1^0 \qquad (19)$$

where δV_1^0 is the change in partial molar volume of the sorbate on transfer from the liquid to the gas phase. Thus, whereas two sorbates may have practically identical retention characteristics ($\Gamma_1 = \Gamma_2$) at low pressures, it is possible to obtain a selectivity coefficient ($k_S = \frac{\Gamma_2 - \Gamma_1}{\Gamma_1}$) large enough for sharp separation by raising the pressure, provided that the δV_1^0 values for the two sorbates are sufficiently different. Integration of Eqn. (19) gives

$$k_s = -P\Delta(\delta V_1^0)/RT \qquad (20)$$

where $\Delta(\delta V_1^0)$ is the difference between the δV_1^0 values for the sorbates.

Thus, for example, if $k_S = 0.1$ is taken to give an acceptable separation of the sorbates, a pressure of the order of 500 atm is needed to achieve that value at $T = 300°K$ and for $\Delta(\delta V_1^0) = 5$ cm^3 mole^{-1}.

Of course, the latter expression must be used in conjunction with Eqn. (17), which describes the increase in separation with pressure for a constant selectivity coefficient.

Since increase of pressure is accompanied by an increase in the concentration of the sorbate in the gas phase, and therefore by a decrease in the distribution coefficient, the possibility arises of chromatographic analysis of substances whose volatility is insufficient for elution under normal conditions and also of compounds which are unstable at elevated temperatures.

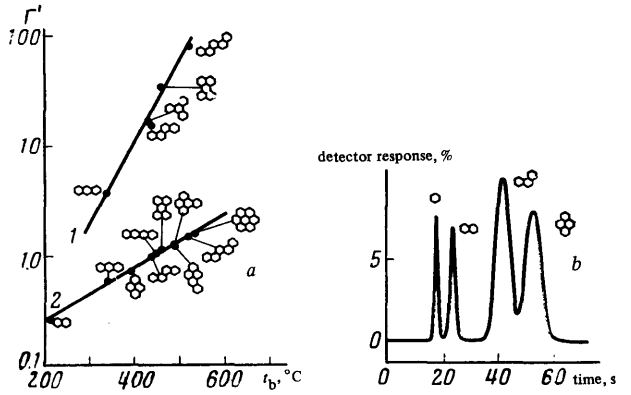

Figure 6. Separation of condensed polynuclear aromatic compounds by fluid chromatography. (*a*) Distribution coefficient against boiling point of the sorbates: *1*) High-temperature (460°) gas chromatography; adsorbent—aluminium oxide treated with NaOH; carrier gas—helium at 1.5 atm. *2*) Fluid-adsorption chromatography at 245°; adsorbent—unmodified aluminium oxide; fluid—isopropanol. (*b*) Fluid-adsorption chromatography; adsorbent—aluminium oxide; temperature 213°; pressure 50 atm.[18,60,61]

Thus, Klesper and coworkers[12] were able to elute from a chromatographic column a mixture of porphyrins, which were thermally unstable at temperatures above 150–170°, by using a mobile phase of Freons under supercritical conditions (150–170°, pressure up to 136 atm). Subsequently, Sie and Rijnders[18,60-62] made a detailed study of eluents (pentane, isopropanol, and diethyl ether) under supercritical conditions, and developed the method of "fluid" chromatography, by which they were able to analyse polynuclear aromatic hydrocarbons and other compounds with boiling points up to 600°. The volatility of the solvates increased by a factor of 10^3–10^4 under their conditions.

Fig. 6*a* shows plots of the coefficient Γ against the boiling point of the sorbate. It is evident that the increase in volatility on going to supercritical conditions is most marked for the heaviest sorbates. The elution of a mixture of benzene, naphthalene, phenanthrene, and pyrene on an aluminium oxide column at 213° and 50 atm (eluent: n-pentane) was completed in ~1 min (Fig. 6*b*).

Giddings and coworkers[13-15] used carbon dioxide and ammonia at supercritical temperatures and pressures up to 2000 atm as eluents. They observed the migration, along a column, of compounds with a molecular weight up to 400 000. The increase in the volatility of the sorbates in this case was of the order of 10^6.

The density of the mobile phase is one of the most important factors determining the solubility of sorbates in the mobile phase‡. Giddings and coworkers[15] considered the relationship between the density of the eluent and its solvent power. They used the Hildebrand solubility parameter[63] δ, whose magnitude can be defined as

$$\delta = 1.25 \cdot P_{cr}^{0.5} \cdot \rho/\rho_{liq}, \qquad (21)$$

where P_{cr} is the critical pressure, ρ is the density of the eluent, and ρ_{liq} is the density of the eluent in the liquid-like state. On reaching the density of the liquid (at pressures of the order of 1000 atm) the solubility parameter reaches its maximum value $\delta_{liq} = 1.25\, P_{cr}^{0.5}$. Assuming δ to be the same for a liquid and for a gas having the density of the liquid,

$$\delta = \delta_{liq} \cdot \rho/\rho_{liq} \qquad (22)$$

Thus, the nature of the eluent and its specific and non-specific interactions with the sorbate play a very important role in high-pressure chromatography, when the solubility of the sorbate in the mobile phase is comparable with its solubility in the stationary phase. For example, when helium is used as the eluent no appreciable change in the volatility of the sorbates is noted up to 2000 atm.[14,15] Migration of Ni-etioporphyrin II and etioporphyrin II has been observed[12] only in dichlorodifluoromethane at 68 atm and monochlorodifluoromethane at 95 atm. These compounds could not be made to migrate in other Freons. Dichlorodifluoromethane has been used also in the analysis of other metal complexes[64]. The use of ethylene as an eluent has been patented[67].

Since the density of the eluent in the supercritical state increases with pressure but decreases with temperature, it is desirable to work at temperatures only just above the critical temperature and at the highest possible pressures. Fig. 7 shows plots of the effect of temperature on the retention of sorbates[18]. Initially, because of the fast decrease in the density of the eluent with temperature, the solubility of the sorbate in the eluent decreases faster than its solubility in the stationary phase (or its adsorbability), and the distribution coefficient increases. At higher temperatures, however, when the density of the eluent has become low enough, the temperature dependence of the solubility of the sorbate in the stationary phase becomes

‡ For this reason, Giddings suggested the name "density chromatography" for this method[15].

predominant, leading to the decrease in retention with increase of temperature commonly observed in chromatography.

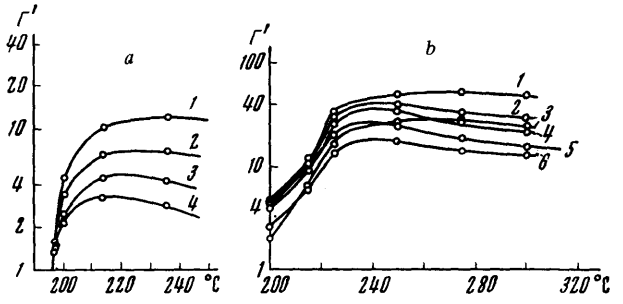

Figure 7. Effect of temperature on the retention of sorbates under fluid chromatography conditions. (*a*) Stationary phase poly(ethylene glycol)-6000 (~23 wt.% on Sil-O-Cel), fluid—n-pentane, pressure 35 atm: *1*) dioctyl phthalate, *2*) dihexyl phthalate, *3*) dibutyl phthalate, *4*) diethyl phthalate[18]. (*b*) Adsorbent—aluminium oxide, fluid—n-pentane, pressure 40 atm: *1*) 10-phenylanthracene, *2*) pyrene, *3*) 1,1-binaphthyl, *4*) 2-phenylnaphthalene, *5*) anthracene, *6*) phenanthrene[60].

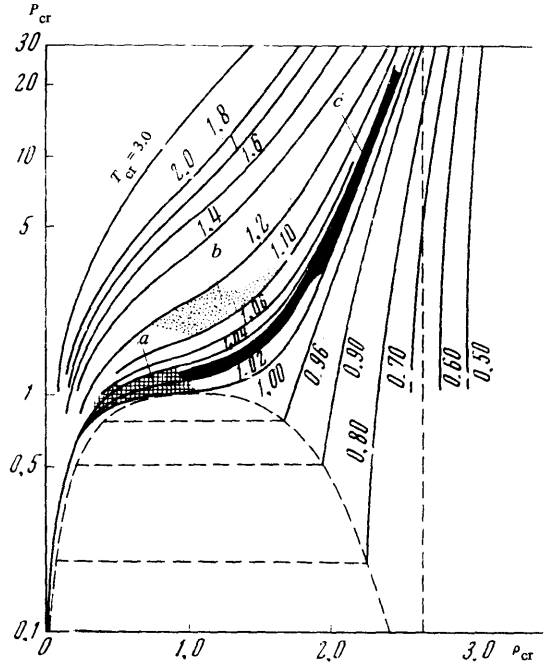

Figure 8. Phase diagram (P_{cr}–ρ_{cr}): *a*) working region of Sie and coworkers[18,60,61], *b*) working region of Klesper and coworkers[12,64], *c*) working region of Giddings and coworkers[13–15].

The diagram shown in Fig. 8 allows the chromatographic conditions used by different workers to be compared. Thus, Sie and coworkers[18,60,61] worked under conditions corresponding to a solubility parameter (δ) for the mobile phase in the range 0.9–2.8. Klesper and his coworkers[12,64] used values of δ between 2.4 and 4.5. On the other hand, Giddings and coworkers[13–15], who worked at pressures up to 2000 atm, obtained gas densities of carbon dioxide (at 40°) and ammonia (at 140°) close to the densities of the corresponding liquids and thus achieved δ values as high as 10. By using these dense eluents they induced migration along the column of compounds such as carotenoids, corticosteroids, nucleotides, carbohydrates, and various polymers. They showed that whereas ammonia (which tends to form hydrogen bonds) has the higher affinity for compounds with hydroxyl and amino groups, carbon dioxide is a better solvent for sorbates showing dispersion and donor–acceptor types of interaction, and can therefore be used to analyse terpenes, polyglycols, esters, alkanes, etc.[13–15] Figs. 9*a* and 9*b* are chromatograms of glycine derivatives and carotenes in dense ammonia and carbon dioxide respectively. The critical parameters of the substances used as eluents are listed in Table 1.

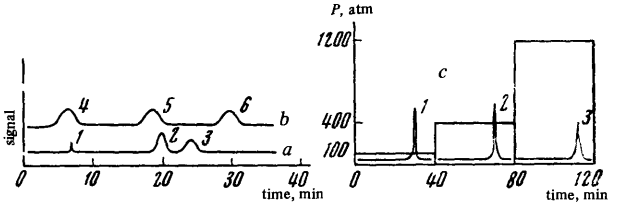

Figure 9. Migration of high-molecular-weight compounds in dense ammonia and carbon dioxide gas. (*a*) Separation in dense carbon dioxide at 500 atm. Column 1.5 m long, filled with 15% of poly(propylene glycol): *1*) air peak, *2*) β-carotene, *3*) α-carotene. (*b*) Separation in dense ammonia at 200 atm. Column 1.5 m long, filled with Porasil B: *4*) glycine, *5*) glycyl glycine, *6*) glycyl-lysyl-tyrosine. (*c*) Separation by a stepped pressure programme, using carbon dioxide at 40°: *1*) squalane, *2*) dinonyl phthalate, *3*) SE-30 silicone rubber (M = 400 000).[13–15]

Table 1. Critical parameters of fluids and working conditions of the columns.

Fluid	T_{cr}, °C	P_{cr}, atm	ρ_{cr}, g cm^{-3}	Working conditions		
				T, °C	P, atm	Refs.
Ammonia	132.3	111.5	0.235	140	< 200	13–15
Carbon dioxide	31.1	75.3	0.468	40	< 2000	13–15
Ethylene	9.90	50.3	0.211	20	100	67
Monochlorodifluoromethane	96	48.71	0.525	150–170	< 136	12
Dichlorodifluoromethane	111.5	40.61	0.558	130–160	< 210	12,64–66
Isopropanol	235.25	47.02	0.2727	245	45–50	18,60–62
Diethyl ether	193.61	36.27	0.2663	200	38–50	62
n-Pentane	196.62	33.31	0.238	213	35–50	18,60–62

By comparing the solvent powers of liquids and dense gases in the liquid-like state (Fig. 10)[14] we may conclude that dense carbon dioxide and ammonia are among the most powerful solvents. Thus, Giddings and coworkers[15] found that in the pentane–carbon dioxide system the solubility parameter δ of the dense eluent could be made greater than the corresponding parameter for the sorbate in the condensed state ($\Delta = \delta/\delta_0 = 1.37$). The same group

showed[15] that a threshold pressure exists at which the concentration of involatile compounds in the mobile phase becomes high enough for detection. Further increase in pressure accelerates the rate of migration of the sorbate.

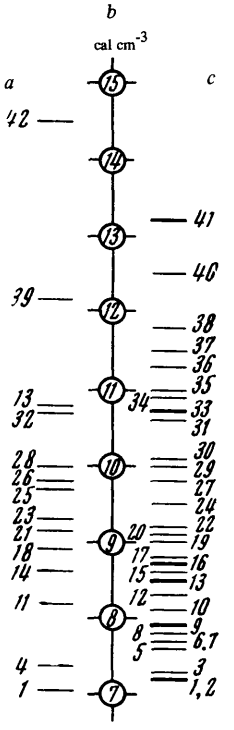

Figure 10. Schematic of (*c*) of the solvent power of gases compressed to a liquid-like state in comparison with (*a*) conventional solvents. (*a*) *1*) n-pentane, *4*) diethyl ether, *11*) cyclohexane, *14*) carbon tetrachloride, *18*) toluene, *21*) benzene, *23*) chloroform, *25*) ethyl acetate, *26*) acetone, *28*) dioxan, *32*) pyridine, *13*) isopropanol, *39*) ethanol, *42*) methanol. (*c*) Gases in the liquid-like state: *1*) n-pentane, *2*) nitrogen, *3*) carbon monoxide, *4*) sulphur hexafluoride.

Thus, in a stream of carbon dioxide the threshold pressure for $C_{18}-C_{36}$ n-alkanes is 87–105 atm, whereas for $C_{11}-C_{18}$ alcohols in a stream of ammonia it is 60–100 atm. Even the substances which are commonly used as stationary phases in gas chromatography can be eluted in a stream of dense carbon dioxide: squalane at 100 atm, dinonyl phthalate at 400 atm, poly(propylene glycol) at 700 atm, SE-30 silicone rubber with a molecular weight of 400 000 at 1200 atm, and Apiezon L at 1500 atm.

Data of this type, describing the migration of various compounds in dense ammonia at 140° and in dense carbon dioxide at 40°, are given in Table 2. At the threshold pressure, the following relationship was observed between the parameter Δ and the distribution coefficient Γ:

$$\Delta = 1 - \left(\frac{RT}{V_1^0\delta_0^2}\ln\Gamma\right)^{0.5} \qquad (23)$$

where V_1^0 is the molar volume of the liquid sorbate.

By analogy with temperature programming for the analysis of substances of widely differing volatilities, a stepwise pressure programme can be devised. Thus, Fig. 9*c* shows a chromatogram for the separation of squalane, dinonyl phthalate, and SE-30 silicone in carbon dioxide, carried out in pressure steps of 40 min duration[15].

Table 2. Migration of various substances in dense NH_3 and CO_2.

Substance	NH_3, 140°, 200 atm	CO_2	
		40°	Pressure, atm
Purines			
Adenine	—	+	1300
Guanine	—	—	1300
Caffeine	++		
Xanthine	—		
Nucleosides and nucleotides			
Adenosine, guanosine, uridine	++	+	1350
Adenylic acid	++		
Corticosteroids			
Cortisone, hydrocortisone	+	+	1300
Sterols			
Cholesterol, ergosterol, lanosterol	++	++	510
Sugars			
Ribose, arabinose, xylose	++	++	1350
Glucose, fructose, mannose, sorbose	++	++	1350
Galactose	+	—	1350
Maltose	++	++	1350
Lactose	++	—	1350
Terpenes			
α-Carotene, β-carotene, lycopene	dec	++	170
Squalene	++	++	510
Amino-acids			
Glycine	++	+	1350
Leucine, tryptophan, tyrosine, arginine, lysine	++	—	1350
Glycyl glycine, glycyl-*L*-leucyl-*L*-tyrosine	++		
Hyppuryl-*L*-arginine	—		
Proteins			
Trypsin, lysosin, apopheritin, γ-globulin	—		
Gelatin	—		
Cytochrome C	+		
Silicone oils and DS-200 rubbers	dec	++	700
OV-1	—		
OV-17	++		
SE-30	—	++	770*
Alkanes			
n-Octadecane, n-docosane, n-octacosane		++	136
Squalane	++	++	90*
Poly(ethylene glycols)			
P.e.g. 400		++	68*
P.e.g. 1000		++	115*
P.e.g. 4000		++	190*
P.e.g. 20000	++	+	
Other substances			
Quercetin	++		
Amygdalin	—		
Polysulphone	—		
Polyox	—		
Polystyrene 900	—		
Versamide 900	—		
Cellulose acetate	—		
L-glucose penta-acetate	++		
Poly(vinyl chloride)		+	1700
Polyethylene		—	1500
Dinonyl phthalate		++	165*
Apiezon *L*	—	++	820*

++Strong migration; + weak migration; —undetectable migration; *threshold pressure.

The choice of mobile and stationary phases for the separation of multicomponent mixtures has been discussed by Sie and Rijnders[18,60,61]. Thus, if the sorption capacity of the stationary phase is high, the elution of homologues is determined by the molecular weight (see *a*, *b*, and *c* in Fig. 11). But if the sorbate and the fluid are polar and the sorbent is non-polar, or vice-versa, the retention characteristics of the homologues become very similar (*d* and *e* in Fig. 11).

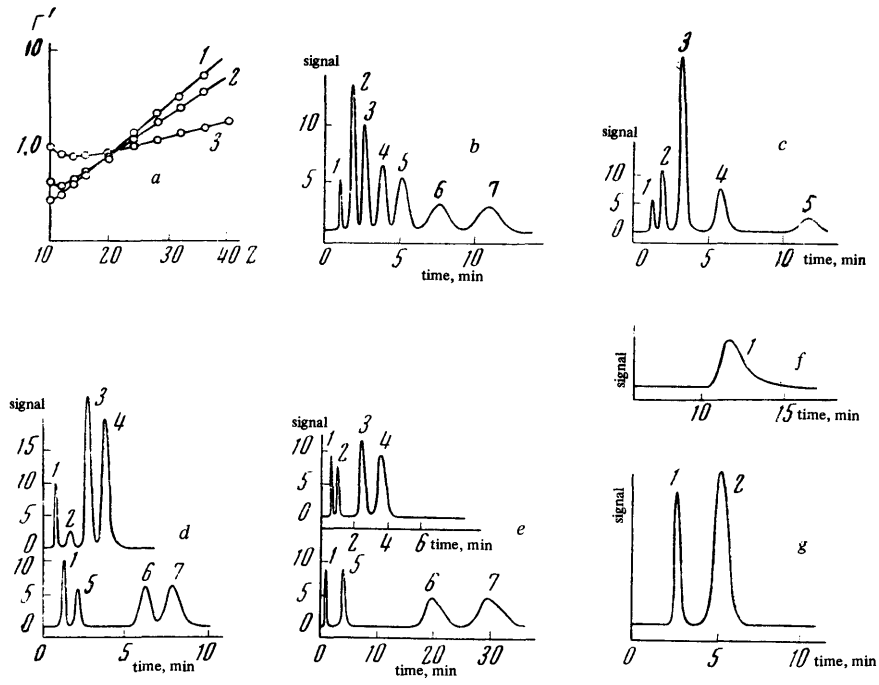

Figure 11. Separation of high-molecular-weight aromatic hydrocarbons in sorbate–fluid–stationary phase systems.

(*a*) Retention of dialkyl phthalates in: *1*) fluid—isopropanol, stationary phase—low-molecular-weight polyethylene; *2*) fluid—n-pentane, stationary phase—low-molecular-weight polyethylene; *3*) fluid—n-pentane, stationary phase—poly(ethylene glycol)-6000. n-Pentane at 213° and 42 atm, isopropanol at 245° and 49.5 atm. Polyethylene (~10 wt. %) and poly(ethylene glycol)-6000 (~23 wt. %) on Sil-O-Cel. *Z* is the number of carbon atoms in the phthalate molecule.

(*b*) Separation of phthalates according to molecular weight. Column length 2 m, inner diameter 6 mm, filled with polyethylene (~10 wt. %) on Sil-O-Cel. Fluid—isopropanol, temperature 245°, pressure 49.5 atm. *1*) Benzene, *2*) dihexyl phthalate, *3*) dioctyl phthalate, *4*) didecyl phthalate, *7*) dihexadecyl phthalate.

(*c*) Separation of some condensed aromatic hydrocarbons on an alumina-packed column. *1*) Benzene, *2*) naphthalene, *3*) phenanthrene, *4*) 1,2-benzanthracene, *5*) picene. Fluid—isopropanol at 245° and 45.2 atm; adsorbent—aluminium oxide.

(*d*) Separation of bi- and triaryl isomers. *1*) Benzene, *2*) biphenyl, *3*) *o*-terphenyl, *4*) *p*-terphenyl, *5*) naphthalene, *6*) 1,1′-binaphthyl, *7*) 2,2′-binaphthyl. Fluid—isopropanol at 245° and 45 atm; adsorbent—aluminium oxide.

(*e*) Separation of close-boiling polynuclear aromatic hydrocarbons. *1*) Benzene, *2*) naphthalene, *3*) phenanthrene (T_b = 336.8°), *4*) anthracene (T_b = 339.9°), *5*) pyrene, *6*) 3,4-benzpyrene (T_b = 495°), *7*) 1,2-benzpyrene (T_b = 493°). Fluid—n-pentane at 200° and 39.8 atm.

(*f*) Shape of the *m*-terphenyl peak (T_b = 364°) under conditions of high-temperature gas-adsorption chromatography. Carrier gas—helium; adsorbent—aluminium oxide treated with NaOH; temperature 350°; pressure 1.5 atm.

(*g*) Separation of *m*- and *p*-terphenyl (T_b = 576°) under conditions of fluid-adsorption chromatography. Fluid—isopropanol at 245° and 50 atm; adsorbent—aluminium oxide[18,60-61].

When considering the retention of sorbates at high pressures it is important to allow for eluent–sorbent interactions. Thus, solubility of the eluent in the stationary phase leads to the formation of a binary phase in gas–liquid chromatography[58]. In the gas-adsorption variant, if both the adsorbent and the eluent are polar the active centres on the surface of the adsorbent are deactivated by eluent molecules, which improves the symmetry of the chromatographic peaks and shortens the elution time. If a non-polar eluent is used, it is possible to add small amounts of a polar substance to the eluent.

In principle, one can define conditions such that the adsorbed eluent acts as a stationary phase and the retention is determined by the difference between the solubility parameters of the sorbate in one and the same compound in the liquid and the gaseous state respectively.

Chromatograms of polyphenyls are shown on Figs. 11*f* and 11*g*. They were obtained at high temperature (350°) on a column packed with alkali-modified alumina, and also by fluid-adsorption chromatography in a stream of isopropanol at 245° and 50 atm in a column packed with unmodified alumina. In the latter experiment, peaks from the heavier hydrocarbon were detected[61]. The influence of modification was observed also with adsorbents consisting of porous polymers[62].

Of course, the range of stationary phases which can be used at high pressures is limited, because of the increase in volatility at high pressure, and the choice of liquid stationary phase must taken account of the threshold pressure (see Table 2). A study of the stability of stationary phases in a stream of dichlorodifluoromethane[64] showed that poly(propylene glycol) and Apiezon M are lost from the column in a few minutes, and SE-52 silicone slowly volatilises. Nitrile silicone rubber was found to be stable up to 210 atm; Kel-F (polytrifluorochloroethylene) and some other phases were not eluted at all.

With pentane and isopropanol as eluents, polyglycols and low-molecular-weight polyethylene were used as stationary phases[18]; silicone rubbers, polysulphone, polystyrene, Apiezon, and some other stationary phases did not migrate in a stream of ammonia[13–15].

Detection can present some serious difficulties when chromatographic analysis is attempted in a stream of dense gas. Kobayashi and coworkers[68–70] used a katharometer and a radioactivity counter (because their sample was radioactive), both working at atmospheric pressure. However, at elevated pressure the use of a katharometer becomes unattractive because of the decreased sensitivity and the noise from density fluctuations and mechanical vibrations. The thermal conductivity of "fluids" is usually not very different from that of the sorbates. Klesper and coworkers[64] used a flow-through spectrophotometer cell working at pressures up to 100 atm.

Sie and coworkers[18,60–62] used a different method of detection. Their apparatus included a condensing system for the eluent, which was then led as a liquid to a quartz u.v. cell sensitive to aromatic compounds.

Lastly, the eluate from the column has been split into two streams[39,71–73], the main stream being discharged to the atmosphere and the remainder led to a flame-ionisation detector. In this method, of course, one must beware of condensation of high-boiling sorbates upstream from the detector. For this reason, Giddings[15] suggests pyrolysis of the eluate, followed by chromatographic or mass-spectrometric analysis of the resulting low-molecular products.

Data on the methods of detection, and also on the methods of introducing the eluent, used by various authors, are listed in Table 3.

IV. DETERMINATION OF PHYSICOCHEMICAL CONSTANTS OF COMPOUNDS BY GAS CHROMATOGRAPHY AT HIGH PRESSURES

Phase equilibria at high pressures and non-ideality of the gas phase can be studied by chromatographic methods only if strict correlations between the unknown parameters and the retention characteristics of the sorbate are available, with due allowance for the effect of pressure on the velocity distribution, on the viscosity of the eluent, and on the distribution coefficient of the sorbate, and also on the solubility of the carrier gas in the stationary phase[34,36,41,55,56,69,71,74–87].

Table 3. High-pressure chromatography conditions.

Expt. No.	Eluent, and maximum column pressure	Method of adding eluent	Method of sample injection	Detector, pressure	Refs.
1	Light gases, 25 atm	Gas cylinder, regulator, valve	Gas pipette, evacuated and filled with sample vapour. Sample injected in a stream of carrier gas	Flame-ionisation detector. Atmospheric pressure	71
2	Light hydrocarbon mixture 68 atm	Gas cylinder, regulator, valve	Piston injector	Katharometer, radio activity detector. Atmospheric pressure	68
3	Isopropanol, diethyl ether, n-pentane, 50 atm	Liquid, entrained by nitrogen, heated to T_{cr}	Pneumatic apparatus with a sample recess. Sample size: 15 μl of 0.1–1 wt.% soln.	Quartz u.v. cell. Eluate in liquid phase. Atmospheric pressure	18 60–62
4	Freons, 210 atm	Compressor	Solution of sample placed on glass piston. Solvent evaporated, piston inserted in sample injector, temperature and pressure raised, valve between injector and column opened	Flow-through spectrophotometer cell operating at column pressure	12 64–66
5	Gases in supercritical state, 2000 atm	High-pressure compressor	Bypass system with high-pressure valves	Flame-ionisation detector. Atmospheric pressure	13–15

For an ideal gas we have the law

$$\alpha = -\frac{K}{\eta} \cdot \frac{dP}{dl}, \tag{24}$$

where α is the linear velocity, η is the dynamic viscosity of the carrier gas, K is the permeability coefficient, dl is an element of length. It follows that the average pressure along the length of the column is

$$p = \frac{\int_0^L P\,dl}{\int_0^L dl} = \frac{\int_{P_0}^{P_1} -\frac{KP^2\,dP}{\eta P_0 \alpha_0}}{\int_{P_0}^{P_1} -\frac{KP\,dP}{\eta P_0 \alpha_0}} = \frac{\int_{P_0}^{P_1} P^2\,dP}{\int_{P_0}^{P_1} P\,dP} = \frac{2}{3} P_0 \frac{(P_1/P_0)^3 - 1}{(P_1/P_0)^2 - 1} = \frac{P_0}{j}, \tag{25}$$

where α_0 is the velocity of the gas at the outlet of the column of length L, j is the pressure gradient factor§ [see Eqn. (4)]. The effective retention volume (corrected for the dead volume of the column and reduced to the mean pressure), which is related to the distribution coefficient of the sorbate between the stationary and the mobile phase, is given by

$$\bar{\bar{V}}_N = (t_R - t_0) V_\alpha J_3^2, \tag{26}$$

where t_R is the retention time of the sorbate, t_0 is the retention time of the non-adsorbed gas, and V_α is the volumetric velocity of the gas at the column outlet. The distribution of pressure along the length of the column is

$$\frac{l}{L} = \frac{P_1^2 - P^2}{P_1^2 - P_0^2}, \tag{27}$$

where the pressure P corresponds to a cross-section at a distance l from the inlet of the column (see Fig. 12).

However, if the pressure is averaged over the dwell time of the sorbate in the column rather than along the length, and noting that $dt = \frac{\Gamma_0}{\alpha} dl$, where Γ_0 is the Henry coefficient[88], the following expression is obtained:

$$\bar{P} = \frac{\int_0^{t_R} P\,dt}{\int_0^{t_R} dt} = \frac{\int_{P_0}^{P_1} -\frac{KP\Gamma_0}{\eta\alpha^2}\,dP}{\int_{P_0}^{P_1} -\frac{K\Gamma_0}{\eta\alpha^2}\,dP} = \frac{\int_{P_0}^{P_1} \frac{P^3\,dP}{\alpha_0^2 P_0^2}}{\int_{P_0}^{P_1} \frac{P^2\,dP}{\alpha_0^2 P_0^2}} = \frac{3}{4} P_0 \frac{(P_1/P_0)^4 - 1}{(P_1/P_0)^3 - 1} = \frac{P_0}{j}, \tag{28}$$

where $j = J_4^3$, and the time-averaged effective retention volume is

$$\bar{V}_N = (t_R - t_0) V_\alpha \cdot J_4^3. \tag{29}$$

It can be shown that $J_3^2 J_4^3 = \chi^2$ [see Eqns. (4) and (25)], and $\bar{P}/\bar{\bar{P}} = J_3^2 J_3^4 = j^2/\chi^2$ [see Eqns. (4), (25), and (28)].

Eqns. (25) and (28) were deduced on the assumption that η and Γ_0 are constant and $P\alpha = P_0\alpha_0$ along the column.

Martire and Locke[75] determined the mean pressure of a non-ideal gas from the expression

$$P\alpha = (P\alpha)_{id}(1 + a_1 P) \tag{30}$$

Here the product $(P\alpha)_{id}$ corresponds to an ideal gas, $a_1 = \frac{B_{22}}{RT}$, and B_{22} is the second virial coefficient in the equation of state for the carrier gas.

In this case integration gives

$$\bar{\bar{P}} = \bar{\bar{P}}_{id} \frac{1 - a_1 P_0 J_3^4}{1 - a_1 P_0 J_2^3} \approx \bar{\bar{P}}_{id}[1 - a_1 P_0 (J_3^4 - J_2^3)] \tag{31}$$

§ In Everett's terminology[56], we assume

$$J_n^m = \frac{n}{m} \frac{(P_1/P_0)^m - 1}{(P_1/P_0)^n - 1}.$$

and

$$j \approx j_{id}[1 + a_1 P_0 (J_3^4 - J_2^3)]. \tag{32}$$

Giddings and coworkers[36] applied Eqn. (30) together with a relationship between viscosity and pressure:

$$\eta = \eta_{id}(1 + b_1 P) \tag{33}$$

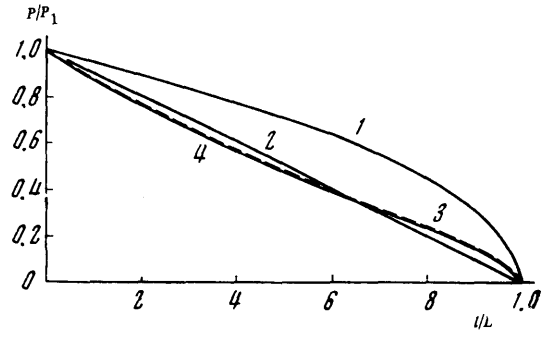

Figure 12. Pressure profile along column. Inlet pressure 1960 atm, outlet pressure 1 atm. *1*) Ideal gas, *2*) liquid, *3*) argon, *4*) nitrogen. Temperature 25°.[41]

The resulting expressions have the form

$$\bar{\bar{P}} \approx \bar{\bar{P}}_{id}[1 - (a_1 + b_1) P_0 (J_3^4 - J_2^3)] \tag{34}$$

and

$$j \approx j_{id}[1 + a_1 P_0 (2J_3^4 - J_2^3 - 1) + b_1 P_0 (J_3^4 - J_2^3)]. \tag{35}$$

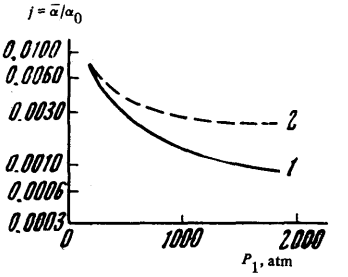

Figure 13. Correction $j = \bar{\alpha}/\alpha_0$ for: *1*) an ideal gas and *2*) nitrogen at pressures up to 2000 atm. Pressure at column outlet 1 atm, temperature 25°. (Constant Γ assumed.)[36]

The pressure profile in real gases is shown[41] in Fig. 12. The quantities j_{id} and j for nitrogen at 25° are compared[36] in Fig. 13. Lastly, Fig. 14 shows[36] the effect of pressure on the ratio $\bar{P}/\bar{\bar{P}}$, which is a correction to the term H in the equation, giving the contribution of diffusion in the gas phase to the height equivalent to a theoretical plate.

The change with pressure of the distribution coefficient Γ of the sorbate can be taken into account by using a linear [55,74]

$$\Gamma = \Gamma^0(1 + \beta P) \tag{36}$$

or a logarithmic [77]

$$\ln \Gamma = \ln \Gamma^0 + \beta P \tag{37}$$

correlation [see Eqn. (18)]. Here Γ^0 is the distribution coefficient extrapolated to zero pressure:

$$\ln \Gamma^0 = \ln \frac{RT}{\gamma_1^\infty V_3 P_1^0} - \frac{B_{11} - V_1^\infty}{RT} P^0, \tag{38}$$

$$\beta = \frac{2B_{12} - V_1^\infty}{RT}, \tag{39}$$

where γ_1^∞ is the activity coefficient of the sorbate at infinite dilution in the pure stationary phase, V_1^0 and V_1^∞ are the molar volume of the liquid sorbate and the partial molar volume of the sorbate at infinite dilution in the stationary phase respectively, V_3 is the molar volume of the pure stationary phase, P_1^0 is the saturated vapour pressure of the sorbate, B_{11} is the second virial coefficient of the sorbate vapour, B_{12} is the second mixed virial coefficient for the interaction between sorbate vapour and carrier gas.

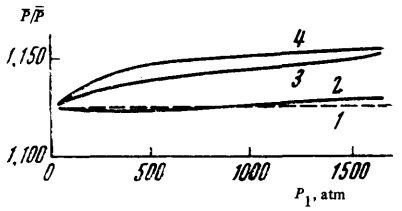

Figure 14. Plots of $\overline{P}/\overline{\overline{P}}$ against pressure at column inlet P_1 for: *1*) ideal gas, *2*) hydrogen, *3*) nitrogen, *4*) argon. Outlet pressure 1 atm, temperature 25°. [36]

Here, and elsewhere in this Review, the subscripts 1, 2, and 3 denote the sorbate, the carrier gas, and the stationary phase respectively.

Windsor and Young [79] obtained an expression for the effective retention volume in terms of the factor β:

$$V_N = \frac{\dfrac{\Gamma^0 V_3 J_3^2}{P_0}\left[\dfrac{e^{\beta P}}{\beta^3}(\beta^2 P^2 - 2\beta P + 2)\right]_{P_1}^{P_0}}{0.5\,[P^2]_{P_1}^{P_0}}, \tag{40}$$

and showed that this expression can be replaced, without significant loss of precision, by a much simpler expression of the type

$$\ln \overline{V}_N = \ln V_N^0 + \beta P_0 J_3^4 \tag{41}$$

(Desty and coworkers [55] used the factor J_3^2, and hence determined the quantity $\overline{\overline{V}}_N$.)

Cruickshank and coworkers [71,80], and also Giddings and coworkers [36], allowed for all three non-ideality factors (a_1, b_1, and β) simultaneously, but their final expressions were unwieldy.

Trestianu [89,91] systematised the published relationships between retention characteristics and column pressure. His results are summarised in Table 4.

Solubility of the carrier gas in the stationary phase is another possible source of variation in retention characteristics. Allowing for this factor, the expression for the effective retention volume at pressures where the third virial coefficient plays a significant role takes the form [80,81,92]

$$\ln V_N = \ln V_N^0 + \beta' P_0 J_3^4 + \zeta' (P_0 J_3^4)^2,$$

where

$$\beta' = \beta + \lambda\left[1 - \frac{\partial \ln \gamma_1^\infty}{\partial x_2}\right]_0,$$

$$\zeta' = \frac{3C_{122} - 4B_{12}B_{22}}{2RT} + \varphi\left[1 - \frac{\partial \ln \gamma_1^\infty}{\partial x_2}\right]_0 + \frac{\lambda^2}{2}\left[1 - \frac{\partial^2 \ln \gamma_1^\infty}{\partial x_2^2}\right]_0 + \frac{kV_1^\infty}{R\Gamma} \tag{42}$$

$\partial\gamma_1^\infty/\partial x_2$ is the change in the activity coefficient of the sorbate in the stationary phase with mole fraction x_2 of dissolved carrier gas, C_{122} is the third virial coefficient for the interaction between the sorbate and the carrier gas, k is a coefficient, λ and φ are constants in the series expansion of the mole fraction x_2 of the carrier gas dissolved in the stationary phase [81]: $x_2 = \lambda P + \varphi P^2 + \ldots$

Table 4. Expressions for j and V_N with allowance for non-ideality of the system [89].

Non-ideality $P\cdot\alpha$	Non-ideality η	Non-ideality Γ	j	V_N	Refs.
—	—	+	J_3^2	$\ln \overline{V}_N = \ln V_N^0 + \beta P_0 J_2^3$	55
—	—	+	J_3^2	$\overline{V}_N = V_N^0(1 + \beta P_0 J_3^4)$	56
+	—	—	$J_3^2[1 + a_1 P_0 (J_3^4 - J_2^3)]$	—	75
+	—	+	$J_3^2[1 + a_1 P_0 (2J_3^4 - J_2^3 - 1)]$	$\ln \overline{V}_N = \ln V_N^0 + \beta P_0 J_3^4$	77
+	+	+	$J_3^2[1 + a_1 P_0 (2J_3^4 - J_2^3 - 1) + b_1 P_0 (J_3^4 - J_2^3)]$	$\ln \overline{\overline{V}}_N = \ln V_N^0 + \beta P_0 J_2^3[1 - P_0 (a_1 + b_1)(J_3^4 - J_2^3)]$ $\ln \overline{V}_N = \ln V_N^0 + \beta P_0 J_3^4[1 - P_0 (2a_1 + b_1)(J_4^5 - J_3^4)]$	36

The general form of the gas solubility correction is

$$\exp\left[\left(\frac{\partial \ln \gamma_1^\infty}{\partial x_2}\right)_0 (\lambda P + \varphi P^2 + \ldots) + \frac{1}{2}\left(\frac{\partial^2 \ln \gamma_1^\infty}{\partial x_2^2}\right)_0 \cdot (\lambda^2 P^2 + \ldots) + \ldots\right].$$

Eqns. (37)–(42) suggest the possibility of determining by a chromatographic method the activity coefficients of sorbates dissolved in the stationary liquid, corrected for the non-ideality of the gas phase (γ_1^∞). Since $V_N = \omega\Gamma$, where ω is the volume of the stationary liquid in the column, the quantity γ_1^∞ can be evaluated by extrapolation of the effective retention volume to zero mean pressure, followed by a correction for the non-ideality of the pure sorbate [second term on the right-hand side of Eqn. (38)]. The mean pressure is expressed as $P_0 J_3^4$.

Chromatographic determinations of activity coefficients from retention characteristics measured at pressures of 12–15 atm (where the influence of the third virial coefficient is not appreciable) have been reported [80,93–101]. Some workers have used several carrier gases in order to achieve greater precision.

The ordinate of the intersection of the linear plots for a single sorbate but different carrier gases (Fig. 15) defines the quantity V_N^0, which is independent of the nature of the chosen eluent. The precision of the chromatographic method of determining γ_1^∞ is evident from Table 5,

where the results are compared with data obtained by the static method.

Locke and Brandt[101] have calculated virial coefficients from the results of experiments at low pressures.

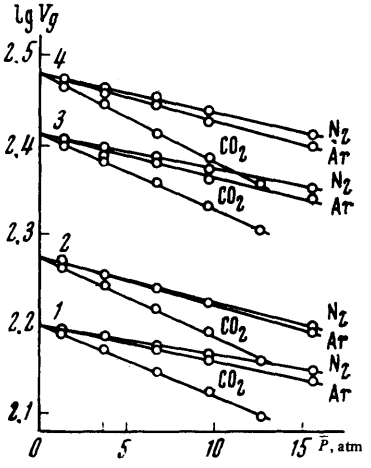

Figure 15. Logarithm of absolute specific retention volume against mean column pressure at 80° in nitrogen, argon, and carbon dioxide for: *1*) dioxan, *2*) n-octane, *3*) toluene, *4*) butyl acetate[73].

Pomazanov and Semkin[102] have determined the activity coefficients of sorbates of different types with a correction for non-ideality of the gas phase, calculated from experiments in columns with a different stationary phase. They were able to show the existence, in an experiment with a homologous series of n-alkanes and a stationary phase of squalane, of a real or hypothetical (i.e. with a non-integral number of carbon atoms) component such that the corrections for B_{11} and B_{12} are mutually compensating and $\gamma^{\infty} = \gamma$.

Table 5. Activity coefficients of hydrocarbons in dinonyl phthalate at 30°. Nitrogen carrier gas[74].

Sorbate	lg γ	lg γ∞	lg γ∞ (static results)
Benzene	—0.250	—0.253	—0.253
n-Pentane	0.022	0.034	0.035
n-Hexane	0.080	0.077	0.076
2,2-Dimethylbutane	0.098	0.103	0.095
Cyclohexane	—0.031	—0.032	—0.032
n-Heptane	0.123	0.117	0.114
n-Octane	0.161	0.153	0.153

Plots like those shown in Fig. 15 enable the second virial coefficients B_{12} for the interaction between sorbates and carrier gases to be determined, since the slope of the linear plot gives the parameter β in Eqns. (37) and (41). Data of this type are not freely available in the literature.

Expanding the compressibility coefficient of the gas mixture in a power series of $1/V$ (where V is the molar volume of the gas mixture)

$$Z = 1 + \frac{B}{V} + \frac{C}{V^2} + \ldots, \tag{43}$$

B and C being the second and third virial coefficient, related to the interaction energy of two and three molecules respectively, we obtain the expression

$$B = x_1^2 B_{11} + 2x_1 x_2 B_{12} + x_2^2 B_{22}, \tag{44}$$

where x_1 and x_2 are the mole fractions of components 1 and 2 in the mixture.

Desty and coworkers[55] used the expression

$$\ln V_N = \ln V_N^0 + \beta P_0 J_2^3, \tag{45}$$

to determine B_{12} for several hydrocarbons mixed with helium, hydrogen, nitrogen, or carbon dioxide in capillary columns with large pressure drops. However, Cruickshank and coworkers have shown[77] that these calculations are subject to large errors and can only be justified if the pressure drop is small. Hence, many other workers have used Eqn. (41) to determine second virial coefficients[72,73,93-96].

Their results (see Table 6) are in good agreement with values obtained by static measurements[103-105]. A number of conclusions regarding the validity of various methods of computing B_{12} have been made from these results. Thus, it has been shown[93,98] that in calculations using the principle of corresponding states the pseudo-critical temperature should be determined by Hudson and McCoubrey's method[107] rather than as the geometric mean of the critical temperatures of the components. It has been shown, also, that Lewis and Randall's rule[108]

$$B_{12} = 0.5(B_{11} + B_{22}) \tag{46}$$

is incorrect.

Semkin and Vigdergauz[73] have noted an approximately linear relationship between B_{12} and the number of carbon atoms in n-alkane molecules, which applies over a range of temperatures and for a number of carrier gases (Fig. 16).

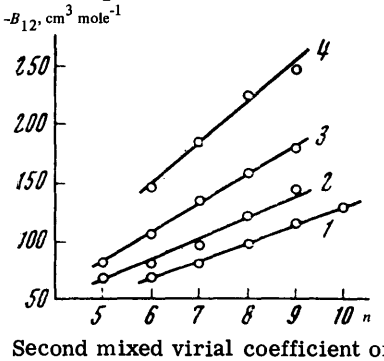

Figure 16. Second mixed virial coefficient of n-paraffins against number of carbon atoms in the molecule. Carrier gas: *1*) nitrogen, 80°, *2*) argon, 80°, *3*) argon, 50°, *4*) carbon dioxide, 80°.[73]

The largest error in the chromatographic determination of virial coefficients arises from the solubility of the carrier gas in the stationary phase. As shown by Everett

Table 6. Second mixed virial coefficients determined by chromatographic and by static methods

Sorbate	Carrier gas	°C	Experimental data: $-B_{12}$, cm^3 mole^{-1}	Experimental data: references	Static data Refs. 103-105: $-B_{12}$, cm^3 mole^{-1}
Acetone	Ar	80	58	72	
	CO_2	40	343	16	
		80	129	72	
Ethyl methyl ketone	N_2	80	36	73	
	Ar	50	86	72	
		80	65	72	
	CO_2	80	184	72	
1,1-Dichloroethane	CO_2	40	215	16	
Chloroform	N_2	80	12	73	
	Ar	50	60	72	
	CO_2	80	59	72	
		80	169	72	
Carbon tetrachloride	N_2	80	24	73	
	Ar	50	125	72	
		80	67	72	
	CO_2	80	154	72	
Nitromethane	N_2	80	41	73	
	Ar	50	91	72	
		80	62	72	
	CO_2	80	188	72	
Nitroethane	N_2	80	71	73	
	Ar	50	125	72	
		80	97	72	
	CO_2	80	247	72	
Dioxan	N_2	80	67	73	
	Ar	50	124	72	
		80	86	72	
	CO_2	80	136	72	
Butyl acetate	N_2	80	79	73	
	Ar	50	138	72	
		80	119	72	
	CO_2	80	260	72	
Methanol	CO_2	40	236	16	
Ethanol	N_2	80	10	73	
	Ar	50	118	72	
		80	46	72	
	CO_2	40	303	72	
		80	95	16	
Isopropanol	Ar	50	80	72	
		80	51	72	
	CO_2	80	127	72	
Propane	CO_2	40	99	16	
n-Butane	N_2	30	78	95	
		35	84	100	
		50	69	95	
		60	77	94.96	
	CO_2	40	153	16	
n-Pentane	H_2	25	−7	55	
			−3	56	
			−2	89	
	N_2	25	105	55	
			76	56	
			103	91	
		30	103	91	
		35	85	100	
		40	85	91	
		55	66	94.96	
		60	80	95	
			72	94.96	
		65	78	94.96	
		80	60	73	
	Ar	25	98	91	136±18
					125±23
		50	82	72	
		80	68	72	
	CO_2	25	173	55	
		40	198	16	
		80	76	72	
	O_2	25	152	55	
	CH_4	25	204	106	222±13
		50	138	106	190±12
	C_2H_6	25	414	106	448±16
n-Hexane	H_2	25	0	55	
			−6	91	
	N_2	25	128	55	
			112	91	
		30	108	95	
		35	113	100	
		40	107	95	
		50	79	91	
		55	90	94.96	
		60	93	95	
			98	94.96	
		65	104	94.96	
		80	69	73	
	Ar	25	124	91	149±65
					80±73
					180±50
		40	104	96	148±27
		50	106	72	108±32
			107	91	120±9
		65	100	91	
		80	81	72	

Table 6 (continued).

Sorbate	Carrier gas	°C	Experimental data: $-B_{12}$, cm^3 mole^{-1}	Experimental data: references	Static data Refs. 103-105: $-B_{12}$, cm^3 mole^{-1}
	CO_2	25	233	55	
		80	147	72	
	O_2	25	163	55	
	CH_4	25	292	106	261±60
		50	280	106	225±30
n-Heptane	H_2	25	36	55	
	N_2	35	132	100	
		40	111	91	
		60	101	94.96	
		75	87	94.96	
		80	81	73	
	Ar	50	136	72	
	CO_2	80	97	72	
		25	294	55	
		80	177	72	
	O_2	25	183	55	
n-Octane	H_2	40	−9	93	
		65.05	−22	93	
	N_2	100			−18±4
		35	143	100	
		60	119	94.96	
		75	92	94.96	
		80	98	73	
	Ar	50	160	72	
		80	122	72	
	CO	40	153	93	
		65.05	123	93	
		100			104±4
	CO_2	80	227	72	
n-Nonane	N_2	80	117	73	
	Ar	50	181	72	
		80	146	72	
	CO_2	80	249	72	
n-Decane	N_2	80	130	73	
Isopentane	H_2	25	−26	55	
	N_2	25	105	55	
		55	64	94.96	
		60	76	94.96	
		65	81	94.96	
	Ar	25	94	91	178±14
		35	78	100	
	CO_2	25	165	55	
	O_2	25	125	55	
	CH_4	25	199	101	
		80	123	101	
2,2-Dimethylbutane	H_2	25	−26	55	
			−9	91	
	N_2	25	105	55	
			88	56	
			94	91	
		35	60	100	
	Ar	25	108*	72	
			115	91	156±26
	CO_2	25	168	55	
	O_2	25	145	55	
	CH_4	25	216	106	
		50	154	106	
Cyclopentane	H_2	25	−5	55	
	N_2	25	91	55	
	Ar	25	108*	72	
	CO_2	25	197	55	
	O_2	25	152	55	
2,3-Dimethylbutane	H_2	25	−9	55	
	N_2	25	112	55	
		35	98	100	
	Ar	25	112*	72	
		35	98	100	
	CO_2	25	208	55	
	O_2	25	153	55	
2-Methylpentane	H_2	25	7	55	
	N_2	25	127	55	
		35	91	100	
	Ar	25	115*	72	147±49
		25	125	91	
	CO_2	25	206	55	
	O_2	25	155	55	
	CH_4	25	317	106	
		50	144	106	
3-Methylpentane	H_2	25	−3	55	
	N_2	25	117	55	
	Ar	25	116*	72	
		35	95	100	
	CO_2	25	211	55	
	O_2	25	163	55	
Methylcyclopentane	H_2	25	12	55	
	N_2	25	128	55	
	Ar	25	127*	72	
	CO_2	25	234	55	
2,2-Dimethylpentane	H_2	25	14	55	
	N_2	25	133	55	
	Ar	25	128*	72	
	CO_2	25	245	55	
2,4-Dimethylpentane	H_2	25	5	55	
	N_2	25	130	55	
		35	109	100	

Table 6 (continued).

Sorbate	Carrier gas	°C	Experimental data: $-B_{12}$, cm^3 mole^{-1}	Experimental data: references	Static data Refs. 103-105: $-B_{12}$, cm^3 mole^{-1}
	Ar	25	130*	72	
	CO_2	25	249	55	
	O_2	25	165	55	
2,2,3-Trimethylbutane	H_2	25	6	55	
	N_2	25	123	55	
	Ar	25	127*	72	
	CO_2	25	222	55	
	O_2	25	160	55	
3,3-Dimethylpentane	H_2	25	12	55	
	N_2	25	131	55	
	Ar	25	132*	72	
	CO_2	25	242	55	
	O_2	25	166	55	
Cyclohexane	H_2	25	18	55	
	N_2	25	120	55	
		35	122	100	
		60	80	94.96	
		80	63	73	
	Ar	25	130*	72	
		50	102	72	
		80	86	72	
	CO_2	25	236	55	
		80	163	72	
	O_2	25	163	55	
1,1-Dimethylcyclopentane	Ar	25	134*	72	
2-Methylhexane	H_2	25	35	55	
	N_2	25	135	55	
	Ar	25	137*	72	
	CO_2	25	272	55	
	O_2	25	175	55	
2,3-Dimethylpentane	H_2	25	6	55	
	N_2	25	133	55	
	Ar	25	135*	72	
	CO_2	25	264	55	
	O_2	25	167	55	
3-Methylhexane	H_2	25	32	55	
	N_2	25	136	55	
	Ar	25	138*	72	
	CO_2	25	276	55	
	O_2	25	180	55	
cis-1,3-Dimethylcyclopentane	Ar	25	136*	72	
trans-1,3-Dimethylcyclopentane	Ar	25	136*	72	
trans-1,2-Dimethylcyclopentane	Ar	25	136*	72	
3-Ethylpentane	H_2	25	36	55	
	N_2	25	144	55	
	CO_2	25	292	55	
	O_2	25	176	55	
2,2,4-Trimethylpentane	H_2	40	—4	93	
		65.05	—6	93	
		75	—		—18±4
	N_2	80	47	73	
	Ar	50	128	72	
		80	87	72	
	CO_2	80	147	72	
n-Pent-1-ene	H_2	35	19	100	
	N_2	35	64	100	
	Ar	35	84	100	
n-Hex-1-ene	H_2	35	13	100	
	N_2	35	110	100	
	Ar	35	110	100	
n-Hept-1-ene	H_2	35	2	100	
	N_2	35	142	100	
		60	95	94.96	
	Ar	35	139	100	
n-Oct-1-ene	Ar	35	136	100	
Buta-1,3-diene	CO_2	40	155	16	
Pyridine	N_2	80	42	73	
	Ar	50	115	72	
		80	95	72	
	CO_2	80	207	72	
Benzene	H_2	25	13	55	
		40	9	96	
		50	9	92	
			5	93	7.5±4
	He	50	—57	93	
			—49	93	
	N_2	20	120	96	
		25	117	55	
			109	94.96	
		30	107	94.96	
		32	103	99	
		35	104	94.96	
		40	96	99	
		40	108	91	
		50	94	96	
			90	99	
			87	93	
		55	86	96	
		60	98	94	
			93	96	
			89	96	
		65	92	96	
		75	79	96	

Table 6 (continued).

Sorbate	Carrier gas	°C	Experimental data: $-B_{12}$, cm^3 mole^{-1}	Experimental data: references	Static data Refs. 103-105: $-B_{12}$, cm^3 mole^{-1}
		80	74	73	
	Ar	35	135	100	
		40	126	96	
		50	117	72	
			90	96	
			79	93	
			88	91	
			85	93	
		65	100	91	
		80	105	72	
	CO	50	113	93	114±4
			122	93	
	CO_2	40	288	16	
		80	216	72	
	O_2	50	79	93	
	CH_4	50	155	93	
Toluene	N_2	80	94	73	
	Ar	50	135	72	
		80	120	72	
			123	58	
	CO_2	80	235	72	
Styrene	N_2	80	117	58	
	Ar	50	169	58	
		80	148	58	
	CO_2	80	300	58	
Fluorobenzene	N_2	32	117	99	
		40	93	99	
		50	96	99	
1,2-Difluorobenzene	N_2	50	95	99	
1,3-Difluorobenzene	N_2	50	97	99	
1,4-Difluorobenzene	N_2	50	94	99	
1,3,5-Trifluorobenzene	N_2	32	110	99	
		40	111	99	
		50	106	99	
1,2,3,4-Tetrafluorobenzene	N_2	50	110	99	
1,2,4,5-Tetrafluorobenzene	N_2	50	105	99	
Pentafluorobenzene	N_2	50	110	99	
Hexafluorobenzene	N_2	32	150	99	
		40	130	99	
		50	111	99	
		55	117	94	
		60	110	94	
		65	108	94	
		75	118	94	

*Obtained by interpolation from retention indices.

and coworkers[93], the solubility of carbon dioxide in octadecane produces an increase of β corresponding to an increase of B_{12} of 75 cm^3 mole^{-1}. When the solubility of the eluent is appreciable, the stationary phase should be treated as a binary system, and the retention characteristics should be determined with the help of expressions derived for multicomponent stationary phases[109,110].

By taking one of the experimental sorbates as standard, it is possible to calculate[88] relative values of $\partial \ln \gamma_1^\infty / \partial x^2$ [see Eqn. (42)]. Thus, ignoring the solubility of the carrier gas, the effective value of the second mixed virial coefficient can be obtained:

$$B_{\text{eff}} = B_{12} + 0.5\lambda \left(1 - \frac{\partial \ln \gamma_1^\infty}{\partial x_2}\right) RT. \qquad (47)$$

Putting $\Delta B = B_{\text{eff}} - B_{12}$, we have

$$\Delta B_{\text{rel}} = \left(1 - \frac{\partial \ln \gamma_1^\infty}{\partial x_2}\right)_{\text{rel}}. \qquad (48)$$

The present writers have shown[87,88] that the retention indices of hydrocarbons[111] are almost linearly related to the mean pressure in the column over a range of pressures extending to at least 30 atm.

We have also proposed[72] an interpolation method of determining B_{12} from values of the retention index I:

$$\frac{\Delta I}{\Delta P} = \frac{(I_1 - 100Z)(\beta_{z+1} - \beta_z) - 100(\beta_x - \beta_z)}{b_2}, \qquad (49)$$

where $\Delta P = P_2 - P_1$, $\Delta I = I_2 - I_1$, I_1 and I_2 are the retention indices of the sorbate at column pressures P_1 and P_2 respectively,

$$\beta_i = \frac{2B_{12i} - V_{1i}^{\infty}}{2.303RT}, \quad i = x, z, z+1, \quad b_2 = \lg \frac{V_{gzP_s}}{V_{g(z+1)P_s}}$$

The latter quantity is the logarithm of the relative retention volume of n-alkanes differing by one carbon atom at pressure P_2, and i is the number of the sorbate.

Eqn. (49) allows the B_{12} coefficients to be determined with high precision if the B_{12} values for two normal alkanes are known. This method has been used to determine the second mixed virial coefficients for the interaction between the carrier gas and the components of a directly distilled light petroleum fraction (see Table 6).

In general, the best results are obtained by the interpolation method when the chosen standards are similar in structure to the experimental sorbates, because under these conditions the adverse influence of the solubility of the carrier gas in the stationary phase is minimised. Thus, benzene and styrene were chosen in a study[58] of aromatic hydrocarbons with carbon dioxide as carrier gas and poly(ethylene glycol)-400 as the stationary phase.

The calculation was made by means of the formula

$$\frac{\Delta G}{\Delta \bar{P}} = \frac{\beta^{(x)} - \beta^{(1)} - G_1(\beta^{(2)} - \beta^{(1)})}{(\lg V_N^{(2)} - \lg V_N^{(1)})_2}, \qquad (50)$$

where

$$\Delta G = G_2 - G_1, \quad \Delta \bar{P} = \bar{P}_2 - \bar{P}_1,$$

$$G = \frac{\lg V_N^{(x)} - \lg V_N^{(1)}}{\lg V_N^{(2)} - \lg V_N^{(1)}},$$

and the superscripts (x), (1), (2) correspond to the experimental sorbate and the two standard compounds. G_1 corresponds to pressure P_1, G_2 and $(\lg V_N^{(2)} - \lg V_N^{(1)})_2$ correspond to pressure P_2, and $\beta = \frac{2B_{12} - V_1^0}{2.303R}$.

The values of B_{12} obtained for alkylbenzenes are given in Table 7.

We have also proposed an interpolation method of calculating B_{12} from the linear retention index[115]

$$J = \frac{t_{Rx} - t_{Rz}}{t_{R(z+1)} - t_{RT}} + Z. \qquad (51)$$

An expression relating B_{12} to the change of linear retention index with pressure ($\Delta J/\Delta \bar{P}$) was obtained.

By analogy with the calculation based on logarithmic interpolation [Eqn. (50)], a relationship between $\Delta Q/\Delta \bar{P}$ and B_{12} was derived for compounds of similar structure on the basis of the function

$$Q = \frac{t_{Rx} - t_{R1}}{t_{R2} - t_{R1}} \qquad (52)$$

Here t_{R1} and t_{R2} are the retention times of the standards 1 and 2.

Very similar results were obtained by the two interpolation methods of calculating B_{12} (the linear and the logarithmic retention index method). This points to the desirability of using the simpler, linear functions J and Q.

Kobayashi and coworkers[68-70,82-84,112-114] studied gas–liquid equilibria in multicomponent systems including gaseous and liquid hydrocarbons. Their method consisted in introducing into a flowing mixture of sorbates a sample of an individual sorbate, either radioactive (using a radioactivity detector) or non-radioactive (using a katharometer detector). The distribution coefficient of the k-th component, equal to the ratio of its mole fractions in the gas and the liquid phase, was defined as

$$K_k = \frac{y_k}{x_k} = \frac{ZRTV_{liq}}{PV_N\left(1 - \sum \frac{y_i}{K_i}\right)}, \qquad (53)$$

where Z is the compressibility coefficient of the gas mixture, V_{liq} is the total number of moles of the liquid phase, and $\Sigma \frac{y_i}{K_i}$ is the sum of the ratios for all the components except the k-th.

Table 7. Second mixed virial coefficients (for 80°) obtained by interpolation using Eqn. (50).[58*]

Carrier gas	Ar	CO_2
Sorbate	$-B_{12}$, cm^3 mole^{-1}	$-B_{12}$, cm^3 mole^{-1}
Toluene	123	248
Ethylbenzene	138	271
p-Xylene	143	284
m-Xylene	141	282
Isopropylbenzene	148	286
o-Xylene	146	289
n-Propylbenzene	152	292
1-Methyl-3-ethylbenzene	154	309
Isobutylbenzene	159	–
1,3,5-Trimethylbenzene	160	325
s-Butylbenzene	160	312
1-Methyl-2-ethylbenzene	158	310
1,2,4-Trimethylbenzene	156	340
1-Methyl-3-propylbenzene	167	328
1-Methyl-2-isopropylbenzene	168	329
1-Methyl-4-propylbenzene	169	318
1,4-Diethylbenzene	168	342
n-Butylbenzene	168	345
1,3-Dimethyl-5-ethylbenzene	173	348
1-Methyl-2-propylbenzene	171	327
1,2,3-Trimethylbenzene	165	335
1,4-Dimethyl-2-ethylbenzene	174	348
1,3-Dimethyl-4-ethylbenzene	174	350
1,2-Dimethyl-4-ethylbenzene	177	354
1,3-Dimethyl-2-ethylbenzene	167	352
1,2-Dimethyl-3-ethylbenzene	168	349
1,2,4,5-Tetramethylbenzene	183	376
1,2,3,5-Tetramethylbenzene	183	380
1,2,3,4-Tetramethylbenzene	178	386

*Standard values of $-B_{12}$. With carbon dioxide carrier: benzene 216 cm^3 mole^{-1}, styrene 300 cm^3 mole^{-1}; with argon carrier: benzene 105 cm^3 mole^{-1}, styrene 148 cm^3 mole^{-1}.

The distribution coefficients of the light hydrocarbons have been determined in this way at pressures up to 136 atm.

Thus, gas chromatography at high pressures is potentially a very important technique both for analytical work and for the characterisation of physicochemical quantities such as the non-ideality parameters of the gas phase and the constants of phase equilibria.

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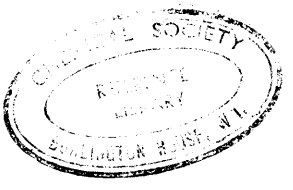

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Factors Determining the Optical Activity of Coordination Compounds

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Investigations of the structure of complex compounds based on analysis of the circular dichroism spectra and the dispersion of optical rotation are surveyed. A list of 124 references is included.

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I. INTRODUCTION

The past five years have seen a tendency to a new, more differentiated use of circular dichroism spectra and the dispersion of optical rotation in the structural study of complex compounds. This approach is based on recognition that the rotational strength of d–d transitions of the complexing metal depends usually not on one but on a number of factors associated with different structural characteristics of the complex molecule. Accordingly, several contributions to the optical activity of a complex can in general be distinguished. Thus the configurational contribution is due to the helical, dissymmetric arrangement of multidentate ligands about the central metal ion. The conformational contribution is due to the asymmetry of an individual non-planar chelate ring. And the presence of asymmetric carbon atoms in the ligand molecule results in the appearance of a vicinal contribution. The establishment of asymmetry in the donor atoms of the ligand (N*, S*) on coordination with the metal can be regarded as a particular case of this last effect.

The additivity of the individual contributions to the optical activity of complex compounds has been proved quite regularly. It is fully justifiable to divide the total effect observed into component parts, and to distinguish each contribution as a differential curve (of the dispersion of optical rotation or, more frequently, of circular dichroism).

In order to study an actual property of a given compound (e.g. the configuration of an asymmetric carbon atom in a ligand) the corresponding differential curve (the curve of the vicinal effect) is, of course, immeasurably more useful than the overall spectrum observed. Moreover, analysis of the overall curve will definitely give misleading information in all cases in which the contributions of the dominant effect and of the effect under investigation are opposite in sign.

The present Review attempts to analyse some possible modes of inducing rotational strength in d–d transitions of metal complexes and to assess their relative effectiveness. Work published during 1964–1969 is covered. Earlier reviews on optically active coordination compounds summarise the literature of the preceding period[1-3]

or discuss only certain particular aspects of this new and promising field of investigation, e.g. present-day theory [4], problems of stereoselectivity [5], the nature of the Pfeiffer effect [6], etc.

Abbreviations often used in the text for various ligands are listed here for the convenience of the reader.

aa	anion of amino-acid
aaH	amino-acid
gly	glycine
ala	alanine
val	valine
leu	leucine
prol	proline
ox	oxalate
mal	malonate
tartr	tartrate
am	diamine
en	ethylenediamine
N-Meen	*N*-methylethylenediamine
pn	propylenediamine
phala	phenylalanine
o-phen	phenanthroline
IDA	iminodiacetate
EDDA	ethylenediaminediacetate
EDTA	ethylenediaminetetra-acetate
TMDTA	trimethylenediaminetetra-acetate
EDTP	ethylenediaminetetrapropionate
hmc	hydroxymethylenecamphor
$(sal)_2pn$	disalicylidenepropylenediamine
N-Meala	*N*-methylalanine
alada	alanine-*NN*-diacetate
tn	trimethylenediamine
chxn	*trans*-cyclohexane-1,2-diamine
tetraen	tetraethylenepentamine
penten	*NNN'N'*-tetrakis-2-aminoethylethylenediamine
sar	sarcosine

II. EFFECT OF CHELATION

Fundamental work on the chemistry of optically active organic compounds indicates that an asymmetric centre induces a quite measurable rotational strength, even if the chromophore is separated from it by two or three carbon atoms [7]. With complexes of unidentate ligands, such as *dextro*-s-butylamine and *dextro*-α-methylbutyric ester, however, the Cotton effect could not be observed in *d–d* transitions of a metal chromophore separated from the asymmetric centre by only one or two atoms [8].

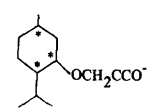
Mercury complexes containing an asymmetric carbon atom directly attached to the metal were investigated on the assumption that the asymmetrising effect falls away with distance more rapidly in coordination compounds than in organic compounds. However, measurements of circular dichroism did not reveal bands above 220 nm with *dextro*-s-butylmercuric bromide, chloride, and quinolin-8-oxide [9]. On the other hand, this was a somewhat unfortunate choice, since the Hg^{2+} ion, in which the d^{10} electron shell is complete, cannot act as a chromophore in the *d–d* range.

A series of papers on transition-metal complexes containing an asymmetric donor nitrogen atom together with other types of asymmetry (configurational, conformational) is not very useful for solving this problem owing to the difficulty of isolating the vicinal effect of the asymmetric donor nitrogen atom from the observed overall curve [10,11].

Nevertheless, it is well known that, in comparison with the above cases of unidentate ligands, bidentate optically active ligands usually induce Cotton effects of considerable amplitude in *d–d* transitions, although the asymmetric centre is sometimes very remote from the chromophore. Still earlier, in 1950, similar observations led Lifschitz [12] to suggest that the induced Cotton effect of *d–d* transitions in complexes of transition metals is of measurable magnitude only if the asymmetry ligand possesses chelating power. This rule might be extremely useful for determining the mode of coordination of potential multidentate ligands in solution. Subsequent investigations indicated that the above statement was too categorical.

From a comparison of the dispersion of optical rotation of the ions $[Co(+)\text{-tartr}(NH_3)_4]^+$ and $[Co(+)\text{-tartr}(NH_3)_5]^{2+}$, which contain bidentate and unidentate tartaric acid respectively, Bhatnagar and Kirshner showed [13] that the two curves are similar in shape, the only difference being that the complex containing the unidentate ligand exhibits half the Cotton effect in the *d–d* region.

Kirshner analysed the contradictory results of this work and that mentioned above [8], and suggested that the increase in optical activity might be due to an increase in the number of asymmetric centres in the optically active ligand. A cobalt(III) complex $[Co(-)\text{-menac}(NH_3)_5](NO_3)_2$, which contains as unidentate ligand the *laevo*-menthoxyacetate ion (I) having three asymmetric centres



(I)

was therefore prepared and examined spectropolarimetrically [14]. The sharp positive Cotton effect in the region of the absorption band due to the cobalt(III) ion in the circular dichroism spectrum is of smaller amplitude than that of the corresponding complex of unidentate *dextro*-tatrate. This result is fully understandable if it is borne in mind that the increase in the number of asymmetric centres was accompanied in this case by considerable remoteness from the chromophore, and that the latter was evidently the dominant factor.

This work was not followed by more correctly designed investigations, and the effect of the number of asymmetric centres on the magnitude of the Cotton effect which they induce remained an open question. Nevertheless, it may be supposed that increasing their number is more likely to produce mutual extinction of their individual contributions with a diminution in intensity of the overall effect.

There is probably a general tendency for the rotational strength of *d–d* transitions to decrease on passing from complexes of bidentate ligands to those of analogous unidentate ligands. This is most clearly demonstrated in an extremely detailed paper by Japanese workers, who investigated complexes of two types—$[Co(NH_3)_4L\text{-aa}]^{2+}$ and $[Co(NH_3)_5L\text{-aaH}]^{3+}$—with bidentate and unidentate amino-acids respectively [15]. The anomaly in the region of the first absorption band of the cobalt(III) ion in the dispersion of optical rotation of complexes of the second type is so weak in comparison with that of their chelate analogues that only qualitative measurements are possible with them. Several reasons may be suggested for such a sharp decrease in amplitude of the Cotton effect on rupture of a chelate ring: the most important are probably [15] the increase in distance between the asymmetric centre and the chromophore—from Co–N–C* for the chelated ligand to Co–O–C–C* for the unidentate amino-acid—and secondly the increase in the conformational mobility of the

ligand—from the rigidly fixed conformation of the chelated amino-acid to a mixture of several conformers of the unidentate ligand—which is due to free rotation of the acyclic molecule.

Since in all the above cases a Cotton effect was observed in complexes of the unidentate ligands, which were in principle capable of chelation, the question of the relation between an anomaly in the visible region and the formation of a metal-containing ring can be finally settled only by examining complexes with truly unidentate ligands. This has been done by Bosnich [16], who isolated a square planar palladium(II) complex *trans*-$[PdCl_2L_2]$ and oxidised it with chlorine to the octahedral palladium(IV) complex *trans*-$[PdCl_4L_2]$, where L represents the optically active unidentate ligand (−)-α-methylbenzylamine. It was obvious from the measured circular dichroism spectra that *d*–*d* transitions of the palladium ions possessed appreciable optical activity in both cases, although here, too, the amplitudes of the Cotton effect were considerably smaller than those usually observed with dissymmetric chelate compounds [17,18].

This result indicates that the rotational strength of *d*–*d* transitions in metal complexes is determined in considerable measure by the remote asymmetric centre of a unidentate ligand, although its interaction with the chromophore is considerably weaker than the effects observed in chelate systems. Attempts to explain the optical activity of complexes of unidentate ligands by any other types of chelation, e.g. outer-sphere chelation [19], appear to the Reviewers quite artificial.

Thus differences in the rotational strengths of *d*–*d* transitions between chelates and the non-chelate type of complexes are only quantitative, not qualitative. This is confirmed by the presence of quite measurable vicinal† effects in almost all complexes of optically active ligands which have now been studied differentially. The main reason for the decrease in rotational strength in the *d*–*d* region on the opening of a metal-containing ring is probably the sharp increase in conformational mobility of the monocoordinated ligand accompanied by considerable mutual extinction of the contributions of the various conformers. Similar effects are well known in organic chemistry [21–23].

An especially significant illustration of this hypothesis is a Japanese study [24] of the dependence of the vicinal effect due to a unidentate ligand—an *ortho*-coordinated α-amino-acid—on its conformational mobility. A substantial increase in the amplitude of the Cotton effect was observed in a series of complexes of the type *cis*-$[Co(L\text{-alaH})X(NH_3)_4]^{n+}$, where the size of the ligand X increases gradually in the sequence

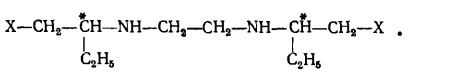
$$H_2O < \text{gly H} < \beta\text{-ala H} < \text{Sar H} < \text{L-ala H} < \text{C-prol H}.$$

This series correlates fairly closely with the restriction of the conformational mobility of optically active unidentate alanine due to its steric interaction with the adjacent ligand X. [24]

This it is evidently no longer possible to suppose that chelation is a necessary condition for the appearance of the Cotton effect in the *d*–*d* region, since it merely increases the rotational strength of these transitions by diminishing the conformational mobility of a unidentate ligand.

†The concept of a vicinal effect was first introduced by Shimura [20].

This conclusion is of both practical and theoretical importance. In practice the rigorous dependence of the induced Cotton effect on the unidentate or multidentate character of the ligand containing the asymmetric centre enables measurements of the dispersion of optical rotation and circular dichroism to be used to study the coordination of potentially multidentate ligands in complexes of undetermined structure



(II)

An example is the determination of the type of chelation of the quadridentate ligand 2,7-diethyl-3,6-diazaoctane-1,8-diol (IIa: X = OH) [25] with copper(II) and nickel(II). Bidentate behaviour of this ligand was simulated by replacing the hydroxyls by chlorine atoms (IIb: X = Cl). This took the asymmetric centres out of the chelate rings, and the centres could contribute to the optical activity mainly by their stereospecific influence on the conformation of the central ethylenediamine chelate ring. The decrease in the amplitude of the Cotton effect by more than 90% on replacement of hydroxyl by chlorine is convincing evidence of the quadridentate behaviour of the ligand (IIa).

A similar principle can be used to determine the mode of coordination of the potentially terdentate ligand cysteine as a function of the acidity of the medium [26].

The copper(II) and nickel(II) complexes of di- and tripeptides provide excellent examples for demonstrating the dependence of optical rotatory power on the number of chelate rings in a complex. Study of the dispersion of optical rotation and the circular dichroism of a series of complex ions with ligands containing a gradually increasing number of potential coordinating atoms showed that the rotational strength of *d*–*d* transitions increases in proportion to the number of chelate rings, with the most highly chelated form possessing the maximum rotational strength [27–29].

This rule is evidently quite general in character, and can be traced in the chelate compounds of metals with diamines and polyamines. The accumulation of metal-containing rings in a complex leads to an increase in optical rotation whether the chelate rings are present in one or more ligands. Thus bisbidentate complexes of the type $[MX_2am_2]^+$ give rotational strengths in the *d*–*d* region double those of the corresponding monobidentate complexes $[MCl_4am]^-$. [30] In the series of complex ions—*cis*-$[Co(NH_3)_2en_2]^{3+}$, $[Coen_3]^{3+}$, $[Copenten]^{3+}$—the amplitude of the Cotton effect, measured from the peak to the trough, increases in the sequence—2200, 7500, 16 000°—in conformity with the presence of two, three, five chelate rings [31].

All these observations demonstrate fairly clearly the same rule: the rotational strength of *d*–*d* transitions of chelate complexes of metals is a function of the number of chelate rings present [32]. This conclusion is of undoubted practical value as a means of studying the coordinating properties of optically active ligands of multidentate type.

Certain theoretical aspects of the relation between the formation of metal-containing rings and the rotational strength of *d*–*d* transitions of the metals can conveniently be noted here. The whole edifice of the modern theory of the optical activity of coordination compounds is based on the necessity of chelation, which produces the dissymmetric departures of the donor atoms in the ligands [33,34], their orbitals [35], or their charges [36] from the regular geometry that are needed for the appearance of the rotational strength of *d*–*d* transitions. Since the chelate

rings are regarded in all cases as the mechanical basis for such deviations, it is undoubtedly of interest to study the effect of the size of the chelate ring on the magnitude of the induced Cotton effect. If the theory is correct, increase in the size of the metal ring should be accompanied by an increase in its flexibility, minimum departures of the donor atoms from their normal positions, and a decrease in the amplitude of the Cotton effect.

A decrease in amplitude of the Cotton effect was actually observed with increase in the length of the carbon chain of the diamine from ethylenediamine to trimethylenediamine in complexes of the type $[Mam_3]^{3+}$, where M = Co^{III}, Cr^{III},[31,37] but this work was followed by several contradictory results[38]. Douglas compared a series of complexes containing a quadridentate ligand (ethylenediaminediacetate) together with carbonate, oxalate, and malonate anions, to give chelate rings containing 4–6 atoms respectively. Contrary to theoretical predictions, all three compounds showed almost identical circular dichroism curves[39]. Moreover, the rotational strength of the complex ion $[Co\,mal_2en]^-$ was double that of $[Co\,ox_2en]^-$, despite the diminution of distortions on the replacement of the oxalate by the malonate ion. Yet the opposite situation is found with the complexes $[Co\,mal_2gly]^{2-}$ and $[Co\,ox_2gly]^{2-}$,[40] and also in a series of complexes of the type $[CoX\,en_2]^+$, where $X = CO_3^{2-}$, ox, mal.[39]

Nor were theoretical predictions confirmed by complexes of multidentate ligands of the type $[CoEDTA]^-$. Diminishing the strain in this system by increasing the size of the chelate rings or by opening them—both diamine rings (in $[CoTMDTA]^-$ and in *cis*-$[CoIDA_2]^-$) and amino-acid rings (in $[CoEDTP]^-$)—did not lead to the expected decrease but to an increase in the intensity of all the bands in the circular dichroism spectrum[41].

These and other similar results[38,42] led to the evident conclusion that it is no longer possible to suppose that the main reason for the optical activity of coordination compounds is the deflection of metal–ligand bonds from their regular geometry as a consequence of the steric requirements of the metal-containing rings. This conclusion receives its most serious support from recent X-ray investigations of optically active complexes[43].

The unnecessary exaggeration of the role of chelation to be found in theoretical and practical papers may be ascribed to the poor sensitivity of the earlier instruments. The impossibility of measuring the Cotton effect induced by unidentate ligands made quantitative differences between chelate and non-chelate systems appear to be qualitative, so that the influence of chelation was erected into an absolute effect. The real reason for the increase of amplitude of the Cotton effect on passing to chelate compounds is the appearance of other contributions to rotation, in addition to the vicinal effect, which result from the specific character of these metallocyclic systems. Such contributions will be discussed in the following Section.

III. CONFIGURATIONAL, CONFORMATIONAL, AND VICINAL CONTRIBUTIONS

The optical activity of octahedral complexes of the type $[M(AA)_3]^{n+}$ or *cis*-$[MX_2(AA)_2]^{m+}$, if the bidentate ligand A is not itself optically active, is a consequence of the exclusively helical arrangement of the chelate rings. This has been termed the *configurational effect*. The examples most often used are cobalt(III)–ethylenediamine complexes —(+)-$[Co\,en_3]^{3+}$ and *cis*-$[CoX_2en_2]^{2+}$—although in general such compounds with non-planar chelate rings contain a contribution from the dominant conformation of these rings besides the purely configurational contribution. It would be far more correct to examine the configurational effect in complexes of planar bidentate ligands such as 1,10-phenanthroline and 2,2′-bipyridyl. Since complexes of the latter type have been known for a long time and have been well studied[44], we shall not discuss the configurational effect in greater detail. We note merely that, since in these cases the metal is both the centre of asymmetry and the chromophore, the Cotton effect in the *d–d* region usually has large amplitudes.

Asymmetric ligand atoms may also cause a Cotton effect whose amplitude is greatly dependent on the distance between the asymmetric centre and the chromophore (the metal ion). This has been termed the *vicinal effect*. It is present in purest form in complexes with optically active unidentate ligands, which have been discussed in the preceding Section. The concept of the vicinal effect includes contributions both by asymmetric carbon atoms in the ligand and by donor atoms (N* in secondary amino-groups, S* in alkylthio-groups) if they become asymmetric on coordination with the metal.

If a ligand forms a non-planar chelate ring on complex formation, an additional, *conformational effect* appears as a consequence of the asymmetry of the individual non-planar metal-containing ring. However, these last two factors are fairly difficult to separate, since formation of the preferred conformer is closely connected with the absolute configuration of the ligand. The two phenomena are often considered together under the concept of vicinal effect[45], although the conformational effect evidently predominates.

Moreover, Larsen and Olsen[8] consider the presence of a Cotton effect in the *d–d* region as proof that the complex contains a non-planar chelate ring with a single dominant conformation: i.e. they attribute the whole of the optical activity to the conformational effect. Such neglect of the vicinal effect cannot be accepted as legitimate if only because there are now sufficient experimental results indicating the presence of strong Cotton effects in the *d–d* region with four-coordinated complexes having completely planar chelate rings. Examples are provided by the dispersion of optical rotation in complexes of (+)-hydroxy methylenecamphor[46] and (–)-α-methylbenzyldithiocarbamic acid[47] containing planar six- and four-membered metal rings respectively.

We shall examine in greater detail these last two effects.

1. Vicinal Contribution

Of all the effects enumerated above the vicinal effect is usually the smallest, as would be expected from the strong dependence of optical activity on the distance between the chromophore and the asymmetric centre.

It would be reasonable to suppose that the largest vicinal effect would be produced by asymmetry of the donor atom of the ligand. Organic compounds containing an asymmetric nitrogen atom are fairly exotic and difficultly accessible owing to the rapid inversion of this centre. On coordination of a secondary amino-group, however, the nitrogen is far more basic than in organic quaternary ammonium salts. This has made possible the resolution into N* enantiomers of several coordination compounds of cobalt(III),[48–51] platinum(II), and platinum(IV)[52] with *N*-substituted diamines and amino-acids.

The optical activity of complexes of the type *trans*-$[MX_2(LL)_2]^+$ with *N*-substituted diamines and amino-acids is assumed to be due solely to the vicinal effect of the asymmetric donor nitrogen atom [48]. This is not altogether true, since it disregards the conformational contribution of the ligand, which is quite large with diamines. Separation of conformational and vicinal contributions and their separate examination is the more important as cases are known in which the absence of information on their relative roles has led to assignment of an incorrect configuration to the complex ion, as has occurred e.g. with the (−)-*trans*-*trans*-$[CoX_2N\text{-Meen}_2]^+$ ion [53].

A similar type of mistake is usually made in discussing the optical activity of *trans*-complexes of optically active diamines in which the nitrogen is unsubstituted [54]. However, this does not lead to large errors, since the C*-vicinal contribution is substantially smaller than the conformational effect, which does not apply to the N*-vicinal contribution.

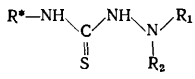
If it is supposed that the circular dichroism of *trans*-$[CoCl_2(S)\text{-pn}_2]^+$ can simulate satisfactorily the contribution of the δ-conformation of coordinated *N*-methylethylenediamine, subtraction of its circular dichroism spectrum from the circular dichroism curve of the (−)-*trans*-*trans*-$[CoCl_2N\text{-Meen}_2]^+$ ion leaves the almost pure vicinal effect of the R–N* asymmetric centre as the resulting curve. The curves obtained in this way show that the N*-vicinal and conformational effects are comparable in magnitude and opposite in sign [55].

The abrupt change in the circular dichroism spectra on passing from ordinary amino-acids to L-proline in complexes of the type $[Cu(L\text{-aa})_2]$ has been attributed to the asymmetry of the donor nitrogen atom [56]. Molecular models make it obvious that only one of the two possible enantiomeric N* configurations can be realised, owing to the steric requirements of this cyclic ligand. This assumption has since been confirmed by X-ray examination [57]. The vicinal effect of the asymmetric nitrogen atom in the coordinated L-prolinate ion results in more intense dichroic bands of certain other complexes, e.g. the $[Co(NH_3)_4L\text{-prol}]^{2+}$ ion. [58] Similar effects are observed in copper(II) complexes containing pseudoephredine and sarcosine [59].

Additional asymmetry, associated with the coordination of secondary amino-groups [60] or alkylthio-fragments of the molecule [61–63], may appear on complex formation by metals with linear multidentate acyclic ligands such as tetraethylenepentamine and also with macrocyclic multidentate ligands [64].

The vicinal effects of asymmetric centres of the carbon skeleton of the ligand which are more remote from the chromophore are substantially smaller than the contributions by asymmetric donor atoms (N*, S*), and this is fully consistent with Chugaev's vicinal rule [65]. An asymmetric α-carbon atom in such ligands as amino-acids develops a far larger vicinal effect than does a β-atom in a side-chain outside the chelate ring. A good illustration of this conclusion is the close similarity in the circular dichroism spectra of the two complexes of the type $[Cu(L\text{-aa})_2]$ in which the amino-acid is respectively L-threonine and L-allothreonine: these amino-acids are respectively *threo*- and *erythro*-isomers, having the same configurations of the α-carbon centres and opposite configurations of the β-atoms [56].

In view of the strong dependence of the vicinal effect on the position of the asymmetric centre in the ligand Lifschitz [12] postulated in 1950 that a necessary condition for the appearance of anomalous dispersion of optical rotation of inner-complex compounds is the presence of an asymmetric carbon atom in the chelate ring. This statement is shown to be too categorical by the work of Jensen [66], who investigated nickel(II) complexes of a series of optically active thiosemicarbazides of general formula



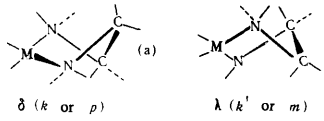
(III)

in which the optically active radical R* is isolated from the chelate ring by a nitrogen atom. Nevertheless, if the α-carbon atom in the radical R* is asymmetric, the circular dichroism spectra indicate quite large rotational strengths of *d*–*d* transitions. Although the reasons for the unusually effective asymmetrising influence of the ligand are not altogether understood [67], the optical activity may be supposed to be due mainly to the vicinal contribution, which merits the closest attention and study.

In view of the important part played by the vicinal effect it is undoubtedly useful in all cases to break down the observed curve of dispersion of optical rotation or circular dichroism into individual contributions, since it will give a clearer idea of several of the finer structural features of the molecules of complex compounds. Furthermore, in individual cases it is possible by means of the curves representing the vicinal effect to obtain a clearer resolution of the components of the *d*–*d* bands than when curves representing the configurational or the total effect are used [68].

2. Conformational Contribution

A consequence of the non-planarity of diamine and certain other chelate rings is the possible formation of at least two conformers of ions of the type *D*-$[Coam_3]^{3+}$. [69,70] In the most stable of them, denoted since Bailar's time as *Dkkk* or lel, all the C–C bonds of the carbon skeleton of the diamines are parallel to the axis of the C_3 complex, and a methyl group (e.g. in *laevo*-propylenediamine) is in the equatorial position. In the less stable isomer *Dk'k'k'* or ob the C–C bonds are oblique. Recently the symbols δ and λ, and also *p* and *m*, have been used most frequently in conformity with the *k* and *k'* notation for enantiomers (IVa, b). [71]



(IV)

However, the situation is evidently not so simple, as is shown by a recent theoretical calculation of conformational energies for ethylenediamine, propylenediamine, and *N*-methylethylenediamine. With ethylenediamine several energetically equivalent symmetrical and unsymmetrical conformations of minimum energy proved to be possible besides the two conformations (δ and λ) recognised by modern theory. Introduction of a methyl group attached to a carbon atom (in propylenediamine) or to a nitrogen atom (in *N*-methylethylenediamine) greatly restricts the number of possible conformations, owing to their strong steric inteacction.

The existence of two principal conformers has been brilliantly confirmed by the X-ray examination of a series

of optically active coordination compounds [43]. It is interesting that, not only the solid state but also in solution, even at room temperature, the predominant conformation of the (−)-propylenediamine chelate ring is the λ-gauche form. This has been shown by a study of the nuclear magnetic resonance spectra of certain platinum(II), palladium(II), and cobalt(III) bis-complexes [73].

Inspection of the literature indicates that the conformational effect of a ligand in a chelate ring depends mainly on the degree of distortion of the latter, on its departure from planarity. In a series of trisdiaminecobalt(III) complexes, for example, the increase in intensity of the circular dichroism bands in the series of ligands—en < pn < chxn—corresponds to the sequence of increasing distortion of the chelate ring by the substituents [74]. The spatial requirements of the ligands increase in the same sequence, and limit the number of possible conformers owing to the sharp increase in the energy differences between them. The diminution in conformational mobility leads to a smaller mutual extinction of the contributions from individual conformations, and hence an increase in intensity of the bands in the circular dichroism spectrum.

The conformational effect, together with the vicinal effect, which is difficult to separate from it, constitutes the basis of the optical activity of *trans*-biscomplexes, such as e.g. *trans*-$[RhCl_2(R\text{-pn})_2]Cl$ and $Na[RhCl_4R\text{-pn}].H_2O$. [75] The Cotton effect in the former complex is double that in the latter, in proportion to the number of chelate rings in the molecule.

An interesting system for studying conformational effects is provided by Schiff bases obtained from optically active diamines and aromatic *o*-hydroxy-aldehydes or -ketones. Examination of the optical rotatory dispersion and the circular dichroism of complexes of copper(II) and nickel(II) with quadridentate Schiff bases of general type $[MSal_2(-)\text{-pn}]$ revealed that the addition of a methyl group to the azomethine carbon atom results in inversion of the signs of the dichroic bands in the region of d–d transitions and a substantial increase in their intensity [76]. Inspection of molecular models showed that, whereas in complex ligands based on aldehydes the δ-conformation of the central diamine chelate ring, with a pseudo-equatorial position of the methyl group of the (−)-propylenediamine, is the preferred conformation, *o*-hydroxyacetophenone gives preference to the (axial-methyl) λ-conformation owing to steric interaction of the two methyl groups. The reversal of sign of the Cotton effect indicates a displacement of the conformational equilibrium $\delta \rightleftharpoons \lambda$ in favour of the latter. It is important to note that the absolute configuration of the diamine plays no part: i.e. the conformational effect predominates greatly over the vicinal effect [76].

Metal complexes of Schiff bases obtained from (−)-*trans*-cyclohexane-1,2-diamine and (−)-propylenediamine provide another example of the predominance of the conformational over the vicinal effect. The circular dichroism spectra of the two series of complexes are enantiomeric, although the configurations of the diamines are the same, RR and R respectively, so that their vicinal contributions have the same sign. The reason for the reversal of sign of the Cotton effect is that the δ-conformation is fixed in the case of the cyclic diamine, whereas the equilibrium in the second case is displaced in favour of the λ-conformation owing to steric interaction between the methyl group of (−)-propylenediamine and the radical R attached to the azomethine carbon atom. The shift in the equilibrium is greater the more bulky the substituent in the R–C(H)=N group. The decrease in such steric interactions in systems containing five-membered chelate rings formed by Schiff bases with pyrrol-2-aldehyde leads to complete similarity of the circular dichroism spectra of complexes based on the two diamines—(−)-propylenediamine and (−)-*trans*-cyclohexane-1,2-diamine [77].

Chelate rings formed by amino-acids were regarded for a long time as almost flat. However, X-ray examination revealed a slight departure from planarity, e.g. in $[Cu(D\text{-ala})_2]$. [78,98] A consequence of the almost planar character of such chelate rings is a marked decrease in their conformational contribution [79,90].

The construction of Dreiding models reveals that even these slight departures of the chelate ring atoms from planarity makes the *k*-conformation of the chelate rings more stable in $[Co(L\text{-ala})_3]$, in which the N–C–C–O chain forms a segment of a left-hand helix, while the methyl groups become quasi-equatorial, which diminishes their mutual steric repulsion [81]. In the *k*′-conformation a bulky substituent occupies an axial position, and the stability of such a conformer is lowered.

Even with greatly flattened amino-acid chelate rings the conformational contribution greatly predominates over the vicinal effect. This has been shown especially successfully by Wellman [82,83], who investigated mixed amino-acid complexes of bivalent copper of general composition Cu : gly : L-aa = 1 : 1 : 1. By displacing the equilibrium $\delta \rightleftharpoons \lambda$ towards the more stable δ-conformer (quasi-equatorial), e.g. by introducing bulky substituents R into the amino-acid or by fixing the second possible conformation λ (quasi-axial) by means of apical interactions of a third donor group with the metal in terdentate amino-acids such as L-histidine and L-$\alpha\gamma$-diaminobutyric acid, this worker demonstrated a reversal of sign and a change in magnitude of the Cotton effect depending on the conformation of the chelate ring, irrespective of the absolute configuration of the ligand, which remained constant.

Thus published results indicate that, of the two effects discussed here—the C*-vicinal and the conformational effects—the latter usually predominates strongly both in diamine and in amino-acid complexes. The vicinal effect of donor atoms (N*, S*) is probably comparable with it in magnitude.

3. Additivity of Contributions and Their Separation

All three effects discussed above—configurational, conformational, and vicinal—are essentially additive, and this applies to the most varied optically active coordination compounds, including various types of chelate rings and different metal ions [80].

The additivity of the contributions makes it entirely legitimate and justified to separate the overall curve observed—of optical rotatory dispersion or circular dichroism—into components corresponding to the individual contributions. The differential curves thus obtained are far more useful for discussing specific details of molecular structure than is the overall spectrum, which represents several such properties. For example, the C*-vicinal effect is uniquely useful for determining the absolute configuration of a coordinated ligand. No error is involved in using the observed spectrum—comprising configurational, conformational, C*-vicinal, and sometimes N*-vicinal contributions—only provided that all the contributions have the same sign, so that sometimes this method cannot guarantee freedom from errors.

Study of the conformational features of a ligand can reasonably start from the curves of the conformational contributions. However, the overall chirality of a com-

plex can be deduced absolutely rigorously only from the purely configurational effect.

Graphical methods are used to isolate individual contributions from the overall curve which is observed. This is effected most simply and conveniently by comparing the circular dichroism spectra with the optical rotatory dispersion curves.

When the circular dichroism spectra of the (+)- and (−)-$[Co\,en(laevo\text{-}pn)_2]^{3+}$ ions are added, for example, the configurational effects for right-hand and left-hand helices, equal in magnitude and opposite in sign, cancel each other out. The resultant curve represents the vicinal effect of four optically active coordinated ligands, and its reduction to one-quarter gives an idea of the vicinal effect of one *laevo*-propylenediamine chelate ring [70]. Subsequent subtraction of the vicinal effects of one, two, or three *laevo*-propylenediamine groups from the experimental circular dichroism spectra of the complex ions—(+)-$[Co\,en_2 laevo\text{-}pn]^{3+}$, (+)-$[Co\,en(laevo\text{-}pn)_2]^{3+}$, or (+)-$[Co(laevo\text{-}pn)_3]^{3+}$—will yield curves of the configurational contribution which, as was to be expected, are closely similar in form and amplitudes of the Cotton effect and resemble the circular dichroism spectrum of the (+)-$[Co\,en^3]^{3+}$ ion, whose optical activity is a consequence of the helical arrangement of the chelate rings [70].

Here, as in papers by many other authors, the vicinal effect includes the conformational effect as well as the actual vicinal effect of the asymmetric carbon atom in the diamine. The two contributions are difficult to separate, since the absolute configuration of the diamine determines the preferred conformation of the chelate ring which it forms.

The additivity of the configurational and the vicinal contributions has been shown in a similar manner, and they have been separated for complexes of the type $[Co\,aa\,en_2]X_2$, where D- and L-alanine, D- and L-leucine, and L-phenylalanine have been used as the amino-acid [84]. The good agreement between the circular dichroism spectra of complex compounds simulating individual contributions and the differential curves of these effects obtained by graphical methods can be regarded as proof of additivity. The configurational effect is represented separately in resolved complexes with optically inactive ligands, e.g. in $(+)_{546}$-$[Co\,gly\,en_2]I_2$, and the vicinal effect in racemic complexes with optically active ligands, e.g. in $[CoL\text{-}phala(NH_3)_4]I_2$. The latter contribution may be expressed also by the sum of the circular dichroism spectra of $(+)_{546}$- and $(-)_{546}$-$[CoL\text{-}leu\,en_2]^{2+}$.

Subtraction of the circular dichroism spectrum of the unresolved complex ion (±)-$[CoL\text{-}phala\,en_2]^{2+}$ from the corresponding curves of each enantiomer yields curves which are mirror images of one another and represent the pure configurational contributions of the two helices of opposite chirality. As was to be expected, these calculated curves are closely similar to the circular dichroism spectra of (+)- and (−)-$[Co\,gly\,en_2]^{2+}$ ions, which do not contain a vicinal contribution [84].

As a consequence of the additivity of the contributions the circular dichroism spectrum of $(-)_{546}$-$Ba[Co\,ox_2L\text{-}ala]$ is well reproduced by adding the circular dichroism curves of $(-)_{546}$-$Ba[Co\,ox_2gly]$ (the configurational contribution alone) and unresolved $Ba[Co\,ox_2L\text{-}ala]$ (the vicinal contribution alone). [85]

Nor are the circular dichroism spectra of dextrorotatory and laevorotatory isomers mirror images of one another with tris-amino-acid complexes of cobalt(III), owing to the additional asymmetry of the α-carbon atom of the α-amino-acid, i.e. the presence of a vicinal effect. The two contributions were shown to be additive, and they were separated for complexes with D- and L-alanine [86], L-leucine, and L-proline [67].

Configurational and vicinal contributions are additive also in the case of mixed complexes of the type $[CoL\text{-}aaL\text{-}aa']^{3+}$ [87], although the considerable increase in steric hindrance in the presence of bulky side-chains, e.g. in L-valine, produces some divergence between observed and calculated curves [88].

The vicinal contributions of different optically active ligands in the same molecule of a complex are also additive and independent, as was shown in a study of a series of complex ions of general type *trans*-(*N*)-$[Co\,alada\,aa]$. [87]

In systems which are not complicated by strong steric interactions the vicinal contributions of several asymmetric centres in the same molecule of a multidentate ligand, e.g. an oligopeptide, are also independent. Evidence of their additivity is the excellent agreement between the observed value of $\Delta\epsilon$ for one of the *d*–*d* transitions of the nickel(II) complex of the tripeptide L-ala-L-ala-L-ala (−2.10) and the sum of the $\Delta\epsilon$ values for the complexes with gly-gly-L-ala, gly-L-ala-gly, and L-ala-gly-gly ($\Sigma\Delta\epsilon = -2.08$). [89]

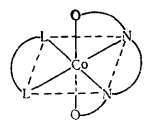
The general rule extends also to the ratio of two—N* and C*—vicinal contributions. In fact the circular dichroism spectrum of $[CoN\text{-}CH_3\text{-}L\text{-}ala(NH_3)_4]^{2+}$ can be reproduced fairly satisfactorily by adding those of the ions $[CoL\text{-}ala(NH_3)_4]^{2+}$ and $(-)_{546}$-$[Co\,sar(NH_3)_4]^{2+}$, representing the vicinal contributions due to the C* and N* centres respectively. The slight discrepancies between the observed and the calculated curve can be explained by the proximity of these two centres and the possibility of some interaction between them [90].

Although the configurational effect and the vicinal effect are far more difficult to separate on the optical rotatory dispersion curves, owing to the more complicated character of the overlapping of individual sigmoid components (inversion curves) corresponding to each optically active absorption band, such work has been undertaken by Japanese [sic] workers [68,91]. From a consideration of the series of complexes—*dextro*-$[CoL\text{-}leu\,en_2]Cl_2$, $[CoL\text{-}leu(NH_3)_4]ClO_4$, *dextro*-$[CoClNH_3en_2]Br$, and *dextro*-$[Co\,en_3]Br_3.2H_2O$—Shimura concluded that the highest molecular rotations in the first of these complexes are due to the fact that the asymmetry about the central metal atom (i.e. the configurational effect) makes a more substantial contribution to the optical rotatory dispersion in the region of *d*–*d* bands than does the asymmetric carbon atom of the coordinated ligand (the vicinal effect). [91]

In this as in most of the investigations mentioned previously the conformational effect was not considered in isolation but together with the vicinal effect. The difficulties of their separation makes even more valuable the use [92] of three complex ions—resolved *cis**-$[CoCl_2^*(NH_3)_2^*en]^+$, unresolved *cis**-$[CoCl_2^*(NH_3)_2^*(-)\text{-}pn]^+$, and optically pure *cis*-$[CoCl_2en_2]^+$—as model compounds in measurement of circular dichroism spectra. In each case the optical activity of the complex is due to mainly one cause—the conformational, vicinal, or configurational effect respectively. The rotational strengths of all three compounds in the same region of *d*–*d* transitions are of the same order of magnitude, although the vicinal effect makes the smallest contribution, and the configurational effect the largest [92].

Isolation of the vicinal contribution from the observed circular dichroism or optical rotatory dispersion spectra has permitted the investigation of the effect of interaction between ligands on the vicinal effect exhibited by the same

ligand in different types of complexes. In effect this work gives indirect information on the conformational component of the total vicinal contribution.



(V)

For example, determination of the vicinal effect of *laevo*-propylenediamine in complexes of the type *trans*-[CoEDDA(LL)]$^+$ (V: LL = en, *laevo*-pn) showed it to be insignificant, contrasting with the fairly large vicinal effect of this ligand in the $[Co(laevo\text{-}pn)_3]^{3+}$ ion [70]. Yet the curves of the vicinal effects of L-alanine in complexes of the type (V: LL = L-ala) and [CoL-ala$_3$] have the same form and differ little in the magnitude of the Cotton effects. Such differences in the behaviour of the two ligands—*laevo*-propylenediamine and L-alanine—when they pass from one type of complex to another are explained by the substantial change in the environment from almost planar amino-acid to distorted diamine chelate rings in the case of *laevo*-propylenediamine, whereas with L-alanine the environment remains almost unchanged [45].

Interligand interactions of this kind probably depend significantly on stereochemical aspects of the environment of the β-carbon atoms in the amino-acids [58].

Thus for the optical activity of d–d transitions in coordination compounds the additivity of the three principal contributions—configurational, conformational, and vicinal—can be regarded as a general rule. The individual contributions can be arranged qualitatively in the sequence —configurational > conformational $\simeq$ N*-vicinal > > C*-vicinal—according to their effect on the intensity of the Cotton effect in this region, which in general yet again emphasises the validity and universality of Chugaev's vicinal rule.

The situation is somewhat more complicated when we consider the optical activity of charge-transfer transitions. Although the individual contributions to the rotational strength of these transitions are additive even in this case, information on the relative roles of each of them is contradictory.

The circular dichroism of trisdiaminecobalt(III) complexes in the visible region (d–d transitions) is an indication mainly of the stereochemistry of the chelate rings arranged about the metal ion (configurational effect). [93] Several investigations suggest that the sign and the amplitude of the Cotton effect due to charge-transfer transitions in the ultraviolet region are given by the sum of the conformational and the configurational contribution, where the former is strongly predominant [39,71,94]. Such predominance was deduced from the fact that the sign of dichroic bands in the region of charge-transfer transitions is determined in many cases solely by the chirality of the diamine chain, irrespective of the absolute configuration of the chelate rings about the metal ion [95]. The presence of both contributions—conformational and configurational—was assumed from a consideration of the optical activity of trisdiamineplatinum(IV) complexes in the region of charge-transfer transitions [96].

The exactly opposite conclusion was reached by Japanese workers [97]. From the opposite signs of the circular dichrosim in charge-transfer transitions (~ 215 nm) for (+)- and (−)-$[Copn_3]^{3+}$ ions having opposite configurations they assumed that the configurational effect is strongly predominant at shorter wavelengths, whereas the vicinal effect predominates at longer wavelengths.

Although the factual information is clearly insufficient to settle this question finally, the conclusions of the first group of investigators seem more reasonable. Actually, Chugaev's vicinal rule indicates that the asymmetry of the metal should determine the optical activity of the internal transitions in the metal (d–d) to a greater extent than transitions of the metal–ligand type (charge-transfer transitions). And conversely, the chirality of an individual chelate ring in the ligand should play the more important part for these latter transitions.

The resolution of the experimental curves representing optical rotatory dispersion and circular dichroism into differential curves corresponding to the individual contributions to the rotation is of undoubted practical value, since it will permit a more correct exploitation of the opportunities offered by spectropolarimetry.

For example, a well known method for determining the absolute configuration of chelate complexes of metals involves comparing their rotatory dispersion or circular dichroism curves with the spectra of complexes whose absolute configuration has been established by means of X-rays. It is quite obvious that, since the configuration of the central metal atom affects only the configurational contribution, the vicinal effects of optically active ligands must be subtracted from the total curve to avoid errors.

On the other hand, vicinal curves obtained by subtracting the configurational contribution from the experimental curve are closely connected with the absolute configuration of an optically active ligand and may provide a means for its determination. Thus the curves of the vicinal effect for *laevo*-propylenediamine and L-alanine have the same general shape, but are mirror images of one another. From this it was concluded that these molecules had opposite absolute configurations [45].

IV. GEOMETRICAL ISOMERISM

Geometrical isomerism is another factor influencing the optical activity of coordination compounds. The elucidation of some generalisations in this field is not only of intrinsic value but also useful as a means for detecting and characterising such phenomena in new systems.

Geometrical isomerism arises in complex compounds of bidentate ligands when the latter are of the unsymmetrical type AB. The possibility of two *cis*- and *trans*-isomers is already apparent in bisamino-acid complexes, although it is rarely taken into account owing to the substantially greater stability of the *trans*-isomer. It is especially interesting that *cis*-[Cu(D-ala)$_2$] has recently been isolated in the solid state, and its structure has been analysed by means of X-rays [98]. However, comparison of the circular dichroism spectra of crystals and solutions of complexes of similar types with other amino-acids showed that the predominant isomer in solution is nevertheless the *trans*-isomer [99].

With amides of amino-acids such geometrical stereospecificity was not so rigorous, and both isomers—*cis* and *trans*—could be isolated in the case of the nickel(II) and palladium(II) complexes of these ligands. The structure of each isomer was assigned on the basis of a study of the effect of solvents on the magnitude, sign, and position

of certain components in the circular dichroism spectrum [100].

The possibility of two geometrical isomers—meridional (mer or 1,2,6) and facial (fac or 1,2,3)—is well known for the trisamino-acid complexes of cobalt(III), rhodium(III), and other metals. Every possible geometrical and optical isomer has been isolated e.g. in the case of the alanine complex $[Co(L\text{-}ala)_3]$. [101]

The differences in the spectropolarimetric behaviour of geometrical isomers are due to their belonging to different symmetry types, resulting in different ways of splitting the bands characteristic of O_h symmetry. For example, the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition is split into two components—of A_2 and E symmetry—in the β-isomers, but into three components—of A_2, B_1, and B_2 symmetry—in the less symmetrical α-isomers. In conformity with this the violet α-isomer of the complex $[Co(L\text{-}ala)_3]$ gives three extrema in the region of the T_1 band in the circular dichroism spectrum, whereas the red β-isomer gives two dichroic components of opposite sign in the same region [81]. The assignment of structures to the α- and β-isomers is supported by nuclear magnetic resonance spectra [67].

Each geometrical isomer exists as two optical isomers, in which the chelate rings are arranged in opposite helices about the metal ion [102]. Thus the total number of isomers of trisamino-acid complexes is increased to four, although this may be greatly diminished by steric hindrance. Thus coordination of the L-prolinate ion yields only one isomer, the fac-Λ-isomer, whose structure has been established by the combined application of electronic spectra, optical rotatory dispersion, and circular dichroism. Similar geometrical and optical selectivity has been observed also with L-hydroxyproline [103].

With terdentate amino-acids the number of geometrical isomers which are theoretically possible is increased to three, each of which occurs as two enantiomers in which the chelate rings are arranged in opposite spirals about the metal atom. Here too, however, steric hindrance reduces the total number of geometrical and optical isomers—to three in the case of D- and L-aspartic acid [104].

Such a terdentate ligand as $\alpha\beta$-diaminopropionic acid, on coordination with cobalt(III) to form a bis-complex, is able theoretically to give five geometrical isomers, three of which are possible only when the two ligands in the complex molecule have the same absolute configuration. In fact it has proved possible to isolate all five isomers with the DL-acid and three isomers with each optically active ligand (D and L). [105]

Geometrical isomerism has hitherto been ignored in connection with bis- and tris-hydroxymethylenecamphor complexes, although the molecule of the chelated ligand has no second-order axis of symmetry and belongs to the AB type of ligands. The most stable was the 1,2,3-isomer, whose structure was confirmed by measuring the nuclear magnetic resonance spectra [106].

Complexes of multidentate ligands of polyamine type [107,108], whose chemistry has been actively developed during recent years, are especially interesting for the investigation of geometrical isomerism. The topology of the coordinated ligand can be in considerable measure controlled by introducing substituents into different parts of the molecule, and the substantial differences in the circular dichroism and optical rotatory dispersion spectra of the various geometrical isomers make these methods, together with nuclear magnetic resonance spectroscopy, especially valuable for structure assignments to individual isomers. However, the number of publications on this topic has recently increased so greatly that the stereochemistry of complexes of multidentate ligands may constitute a subject for a special review.

V. OUTER-SPHERE COORDINATION

The first observations that the molecular rotation of ions of dissymmetric metal complexes depends on the properties of the gegenion were made by Werner as early as 1912. [109] In general this effect is not very large in comparison with those already discussed, but in some cases it plays an important part. An example is the almost tenfold increase in intensity of the dichroic bands due to the (+)-$[Co\,en_3]^{3+}$ ion produced by its outer-sphere interaction with nitrosonaphthoxide ions. The probable reason is strong interaction of the formally forbidden d–d transitions with the charge-transfer transitions which appear on outer-sphere coordination, from which the d–d bands obtain most of their intensity [110].

Most work in this field has been done on the effect of optically inactive ions on the rotatory dispersion or the circular dichroism of optically active complex ions. It is interesting that different transitions are subject to this effect in different degrees depending on their symmetry. Thus the intensity of the positive dichroic maximum corresponding to the $^1A \rightarrow {}^1E_a$ transition in the complex $(+)_{546}$-$[Co\,en_3]Cl_3$ is increased by the addition of all electrolytes other than trisodium orthophosphate, which diminishes the intensity. The negative peak in the circular dichroism spectrum of the same complex ion ($^1A \rightarrow {}^1A_2$ transition) increases in intensity in the presence of all electrolytes, and the orthophosphate anion produces the maximum effect [111].

The effects of trigonal and tetrahedral anions on the optical activity of octahedral complexes of diamines are quite regular. Increase in the concentration of such anions in solution leads in general to a decrease in the rotational strength R of the E_u transition, a compensating increase in that of the A_2 transition, an increase in the rotational strength of the E_g band, and the appearance of a new dichroic component caused by charge transfer from anion to cation.

Quantitative analysis of this latter band has demonstrated the formation in solution of a 1 : 1 ion-pair with complex ions such as (+)-$[Co\,en_3]^{3+}$ and (+)-$[Co(+)\text{-}pn_3]^{3+}$. The main factor in the structure of such an outer-sphere complex is assumed to be a system of hydrogen bonds involving the NH groups of the coordinated diamine molecules [112]. The fact that a similar 1 : 1 outer-sphere complex is not formed with the (−)-$[Co(+)\text{-}pn_3]^{3+}$ ion can be regarded as indirect confirmation of this suggestion. The reason for the marked differences in behaviour of complexes of (+)-propylenediamine having opposite absolute configurations may be the enantiomeric character of the conformations of the chelate rings, only one of which [in the (+)-complex] enables three NH groups to lie in the same direction, parallel to the C_3 axis and convenient for the formation of three NH...X hydrogen bonds with an anion located on the C_3 axis [112].

As a result of this advantage of one of the two conformations the association constants of the lel-$[Co(\textit{dextro}\text{-}pn)_3]^{3+}$ ion were significantly higher than those for the ob-isomer. For example, the values on interaction with the SO_4^{2-} ion were respectively 70 and 43, with *dextro*-$tartr^{2-}$ 30 and 7, and with *laevo*-$tartr^{2-}$ 28 and 16. [113] The differences in the behaviour of *dextro*- and *laevo*-tartrate ions are explained by different relative configurations of the

$^{-}OCO-C-C-COO^{-}$ chain, on its outer-sphere coordination through the two carboxy-groups [114].

The dimeric complex $[Co_2(L\text{-}amO)_3(L\text{-}amOH)_3]^{3+}$ represents a type of association which is rather more complicated than that described above. It is formed by three O–H...O hydrogen bonds between coordinated amino-alcohol molecules L-amOH and their anions $L\text{-}amO^{-}$. [115]

However, the number of possible outer-sphere complexes is not restricted to 1 : 1 products. The above change in the rotational strengths of the components of an octahedral T_{1g} transition is entirely regular for complex ions of many metals—cobalt(III), chromium(III), rhodium(III)—and several anions, such as arsenate, phosphate, selenite, thiosulphate, etc. [116] However, the sign of this effect may be reversed when the concentration of the anion rises above a certain limit. Larsson and his coworkers used similar changes in the circular dichroism spectra to determine formation constants for a series of outer-sphere complexes of general type ML_n, where n = 1–4 when L represented the thiosulphate ion, and n = 1, 2 for the hexacyanoferrate(II) ion. The presence of a maximum effect in the 1 : 1 and 1 : 3 complexes was explained by the fact that formation of a centrosymmetric outer coordination sphere leads to the smallest change in optical activity of the complex cation with even values of n. [117]

In some cases an abrupt change in the circular dichroism spectra is observed only in the third-stage of the formation of outer-sphere complexes, e.g. with *dextro*-$\{[Co\,en_3](SeO_3)n\}^{3-2n}$, [118] or at the third and fourth stages [119].

Analysing possible mechanisms of the effect of outer-sphere coordination on the optical activity of complex ions, Larsson considers that the direct effect of anions on the *d*-orbitals of the metal would be quite small in comparison with the effects observed with inner-sphere coordination. It is most probable that the effect of outer-sphere coordination is indirect—through the mixing of *d*–*d* transitions with the very intense charge-transfer transitions which then arise [117,119].

A second aspect of the same problem is the effect of cations on the optical activity of complex anions. In a study of the molybdate complexes of tartaric and mandelic acids Brown observed that increase in the concentration of simple singly charged alkali-metal cations in the solution was accompanied by an increase in the optical activity, which reached saturation at a certain stage [120]. According to their relative effectiveness the metal ions can be arranged in the sequence

$$Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$$

which is also the sequence of diminishing cationic radius [120].

In order to ascertain which characteristic of an optically inactive ion governs its effect on the optical rotatory dispersion of a complex ion, Albinak [121] made a detailed comparative investigation of the effectiveness of anions (F^-, Cl^-, Br^-, I^-, PF_4^{3-}, SO_4^{2-}, PO_4^{3-}) and cations (Li^+, Na^+, K^+, Rb^+, Cs^+, Mg^{2+}, Ca^{2+}, Ba^{2+}) for a series of salts of two optically active cations (*laevo*-*cis*-$[Co\,ox\,en_2]^+$ and *laevo*-$[Cr\,en_3]^{3+}$) and two anions (*dextro*- and *laevo*-$[Rh\,ox_3]^{3-}$). Comparison of the rotatory dispersion curves within a series showed a clear tendency for the intense long-wavelength rotation maximum to vary with the ratio of ionic charge to ionic size (i.e. the ionic potential) and the polarisability of the optically inactive ion. The plot of molecular rotation against ionic potential is a straight line [121].

A second possibility—coordination of an optically inactive complex ion with an optically active gegenion—has been far less investigated. Mason studied the outer-sphere coordination of hexa-amminecobalt(III) in aqueous solution containing excess of the (+)-tartrate ion, (+)-tartaric acid, or (+)-diethyl tartrate. A completely unexpected result of this work was the discovery of a appreciable Cotton effect in the region of the $^1A_{1g} \rightarrow {}^1T_{1g}$ band, exceeding in magnitude the effect induced in this band by inner-sphere unidentate and even bidentate coordination of the same ligands in the complex ions $[CoL(NH_3)_5]^+$ and $[CoL(NH_3)_4]^+$ respectively. The Cotton effects accompanying inner-sphere and outer-sphere coordination are of opposite sign. The reason for this effect is supposed to be orientation of the species on the surface of the complex ion without elements of symmetry [122].

A similar phenomenon has been noted in the systems formed by the hexa-amminecobalt(III) ion with (–)-α-methylbenzyl acetate [123] and by the tetrachloroplatinate(II) ion with *dextro*-butane-2,3-diol [124].

Outer-sphere coordination is obviously also the cause of the Pfeiffer effect (change in the rotatory dispersion of certain optically active organic compounds, e.g. *dextro*-α-bromocamphor-π-sulphonate and *dextro*-tartaric acid, in the presence of racemic mixtures of certain optically active coordination compounds, e.g. DL-$[Zn(o\text{-}phen)_3]$). This effect was the subject of a recent review by Kirshner [6], and therefore will not be discussed here.

Thus the progress made in recent years in research on optically active coordination compounds gives grounds for hoping that the application of circular dichroism and rotatory dispersion to inorganic chemistry will become increasingly effective, and provide inestimable help in the investigation of those finer aspects of the spectroscopy and the structure of complex molecules to which other present-day methods are insensitive.

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Mechanisms of the Hydroxylation of Aromatic Compounds

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A systematic account is given of various mechanisms for the hydroxylation of aromatic compounds in the liquid phase, and they are discussed critically. Similarities and differences are emphasised in the mechanisms of the action of Fenton's reagent, enzymes, and models of the latter in the hydroxylation of aromatic systems. Mechanisms of radiolytic hydroxylation are examined in detail, and questions concerning the nature of the attacking species and the distribution of the resulting isomeric phenols are discussed. Kinetic data and the mechanism of the hydroxylation of aromatic systems during oxidation together with aliphatic alcohols are examined in detail. A list of 211 references is included.

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I. INTRODUCTION

The concept of "aromaticity" in organic chemistry implies the ability of a substance to undergo substitution readily while being stable to the action of oxidants. This concept arose from a study of the properties of benzene, which, although formally unsaturated, readily undergoes substitution and is very resistant to oxidising agents [1]. The great stability of the aromatic ring in homolytic oxidations is explained also by the fact that benzene and its derivatives do not form the corresponding hydroperoxide, which, by decomposing into free radicals, might have initiated further oxidation. Finally, the oxidation of aromatic compounds yields phenols and their reaction products, which act as inhibitors in the chain oxidation of hydrocarbons.

The direct preparation of hydroxy-derivatives of aromatic compounds in a single stage is of great practical importance, since no effective single-stage process has yet been developed e.g. for obtaining phenol from benzene, there are no methods for producing naphthols by the direct oxidation of naphthalene, and only the direct preparation of anthraquinone from anthracene is of importance in industrial organic synthesis [2]. Yet it is known to be possible in principle to oxidise benzene and its derivatives to phenols under mild conditions: for example, there are enzymes which oxidise phenylalanine to tyrosine; micro-organisms assimilate aromatic compounds, converting them into *o*- and *p*-diols and then cleaving the rings to form aliphatic acids [3]; under certain conditions benzene can be oxidised to give a quite high yield of phenol [4].

We shall not discuss here the oxidation of benzene to phenol in the gas and liquid phases by various methods, since a detailed survey of this question has appeared [4]; nor shall we be concerned with oxidation processes involving destruction of the benzene ring [5]: we shall concentrate our attention on the mechanism of the first stage in the oxidation of aromatic compounds—the hydroxylation of aromatic rings with the formation of phenolic derivatives. In several cases the nature of the hydroxylating agents and the mechanism of their interaction with the aromatic systems are not entirely clear. The aim of the Review is to show the similarities and the differences in the mechanisms of hydroxylation by Fenton's reagent and various catalytic systems which simulate the action of enzymes and the mechanisms of hydroxylation in radiation-chemical processes and also in initiated and combined oxidations involving aromatic compounds. Examination of the mechanisms of the hydroxylation of aromatic compounds will enable a deeper insight to be obtained into processes involving their oxidation and also supplement our knowledge of substitution in the aromatic series.

II. MECHANISM OF HYDROXYLATION BY FENTON'S REAGENT AND ITS ANALOGUES

At a certain ratio of its components Fenton's reagent ($Fe^{2+} + H_2O_2$) is a source of reactive HO· radicals, this being confirmed by its initiation of the polymerisation of vinyl compounds and oxidation of aliphatic and aromatic substances. The following mechanism has now been proved and accepted [6-10] for the interaction of iron(II) ions with hydrogen peroxide:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^- + HO^{\cdot} \quad (0)$$

$$Fe^{2+} + HO^{\cdot} \rightarrow Fe^{3+} + HO^- \quad (1)$$

$$H_2O_2 + HO^{\cdot} \rightarrow HO_2^{\cdot} + H_2O \quad (2)$$

$$Fe^{2+} + HO_2^{\cdot} \rightarrow Fe^{3+} + HO_2^- \overset{H^+}{\rightleftarrows} H_2O_2 \quad (3)$$

$$Fe^{3+} + HO_2^{\cdot} \rightleftarrows Fe^{2+} + H^+ + O_2 \quad (4)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\cdot} + H^+ \quad (5)$$

In the presence of excess of Fe^{2+} ions reactions (0) and (1) take place; with excess of hydrogen peroxide in acid solutions, when reactions (4) and (5) can be neglected, reactions (0), (2), and (3) occur. Comparable concentrations of Fe^{2+} and H_2O_2 in acid media result in reactions (0)–(3). The stoichiometry of the reaction is $2Fe^{2+}$ and H_2O_2. The rate constant of reaction (0) has been given as $k_0 = 4.45 \times 10^8 \exp(-9400/RT)\ M^{-1}\ s^{-1}$. Thus with excess of the Fe^{2+} ion in acid media Fenton's reagent and its analogues are efficient sources of HO· radicals.

A large amount of work has been done on the hydroxylation of aromatic systems by Fenton's reagent and its analogues ($Cu^{2+} + H_2O_2$, $Ti^{3+} + H_2O_2$, etc.). [11-26] Studies have been made of the hydroxylation of benzene [11-15,18,20], naphthalene [21], toluene [18,22,24], anisole [24], fluorobenzene [23], phenol and its substituted derivatives [23,25], nitrobenzene [12], and acetanilide [23].

Early papers [11,15] suggested the following mechanisms of interaction between the HO· radical and an aromatic compound:

$$XC_6H_4H + HO^{\cdot} \rightarrow XC_6H_4^{\cdot} + H_2O$$
$$XC_6H_4^{\cdot} + Fe^{3+} + HO^- \rightarrow XC_6H_4OH + Fe^{2+}$$
$$XC_6H_4^{\cdot} + XC_6H_4^{\cdot} \rightarrow XC_6H_4{-}C_6H_4X.$$

The reaction results in the formation of phenol and biphenyl (derivatives of the latter are not formed in nearly neutral media in the presence of oxygen). If oxidation does involve detachment of a hydrogen atom in conformity with the above scheme, an isotope effect should be observed in the reaction between HO· and completely deuterated benzene C_6D_6, provided that the detachment of a hydrogen or deuterium atom limits the rate of formation of reaction products. However, no isotope effect was observed experimentally in the oxidation of hexadeuterobenzene by Fenton's reagent [18], which indicates either that detachment of a hydrogen atom does not occur or that this step does not limit the overall rate of the process. It is noteworthy that removal of a hydrogen atom may occur to a slight extent with rise in temperature, as is indicated by the increase in k_H/k_D from 1.25 (at 20°) to 1.37 (70°C) in the oxidation of a mixture of ordinary and deuterated benzene [27].

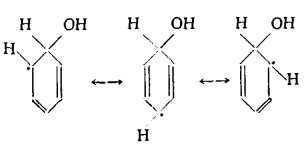
Proskurin and his coworkers [28] were the first to suggest that the HO· radical adds to the benzene ring to form the complex radical $C_6H_6O{\cdot}H$. The existence of this radical was demonstrated by pulse radiolysis combined with flash spectroscopy [29], its absorption spectrum (λ_{max} = 313 nm) has been determined, and the addition rate constant calculated as $(4.3 \pm 0.9) \times 10^9$ M^{-1} s^{-1} at 25°C.

The use of ^{18}O to investigate oxygen transfer in the reaction of benzene with Fenton's reagent and its analogue $Cu^{2+} + H_2O_2$ showed that 15–23% of oxygen is incorporated from water into the phenol if no oxygen is present in the gas phase, and 5% of oxygen from the gas phase if the latter contains oxygen [20]. The results are consistent with the mechanism

$$H_2O_2 + Fe^{2+} \rightarrow HO^{\cdot} + Fe(OH)^{2+}$$
$$C_6H_6 + HO^{\cdot} \rightarrow (C_6H_6OH)^{\cdot} \rightarrow PhOH + H$$

The limiting step is the formation of HO· radicals, not their interaction with benzene.

Dixon and Norman [19] used electron spin resonance to study the free radicals formed in the systems—$H_2O_2 + Ti^3$ and $H_2O_2 + Ti^3 + C_6H_6$—and found that the hydroxy-radicals disappear in the presence of benzene. New radicals appear, to which these workers attributed the structure

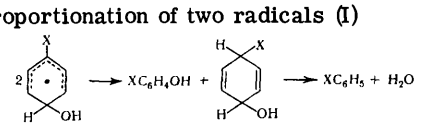


All the above results confirm that the first stage in the reaction between HO· and C_6H_5X (where X is a substituent) is the addition of hydroxyl to the benzene ring with formation of a cyclohexadienyl type of radical. The radical $XC_6H_5O{\cdot}H$ (I) is then able to react in three ways [18]—

(*A*) formation of phenolic compounds

$$I + Fe^{3+} \rightarrow XC_6H_4OH + Fe^{3+} + H^+ \quad (6)$$
$$I + O_2 \rightarrow XC_6H_4OH + HO_2^{\cdot} \quad (7)$$

(*B*) disproportionation of two radicals (I)



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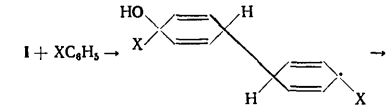
(*C*) formation of biphenyl compounds



(9)

Three mechanisms can be suggested [30,31] for the formation of biphenyl compounds—removal of a hydrogen atom from the C_6H_5X molecule followed by recombination of the phenyl radicals, addition of the radical (I) to C_6H_5X with simultaneous detachment of hydrogen (as shown in scheme *C*), and slow formation of an intermediate complex by addition of the radical (I) to C_6H_5X with a subsequent rapid reaction due to attack by another radical or by the action of an oxidant (HO·, Fe^{3+}, or O_2 with the formation of H_2O, $Fe^{2+} + H^+$, and $HO_2^{\cdot}$ respectively)—among which the third mechanism appears to be the most probable [32,33].

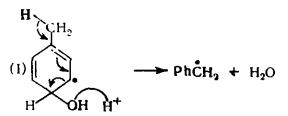
In the presence of oxygen the most probable route for the formation of phenol is reaction of the radical (I) with an oxygen molecule, the rate constant of which is quite large—$(5.0 \pm 0.6) \times 10^8$ M^{-1} s^{-1} at 23°C [34]—so that disproportionation of two radicals (I) (scheme *B*) is improbable. The formation of phenol in preference to biphenyl compounds in the presence of molecular oxygen is explained by the more rapid reaction of (I), with this oxidant than with C_6H_5X (scheme *C*). In the absence of oxygen biphenyl compounds are formed, and also phenol by reaction (1) with Fe^{3+} and by disproportionation (scheme *B*).

Table 1.

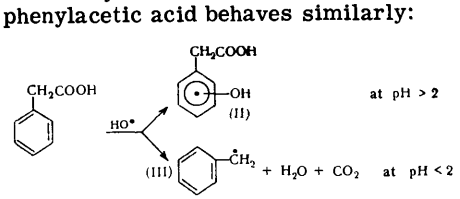
pH	Yield of products × 10^5 (moles)	
	1,2-diphenylethane	cresols
1.3	60	2.7
2.1	16	4.4
3.6	1.5	34

The pH of the medium has a great effect on the rate of oxidation by Fenton's reagent and on the composition of the products. The distribution of isomeric phenolic derivatives is maintained with variation in pH, but the proportions of phenolic and biphenyl products change substantially [24]. Table 1 gives the variation in the composition of the products for the oxidation of toluene.

Large quantities of 1,2-diphenylethane are formed in acid media in the absence of molecular oxygen. This is due to the acid-catalysed conversion of the corresponding cyclohexadienyl radical into a benzyl radical:



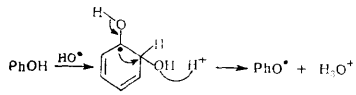
The cyclohexadienyl radical formed by the interaction of HO· with phenylacetic acid behaves similarly:



The radical (III) has been recorded in strongly acid media by electron spin resonance, and the radical (II) in less acid media.

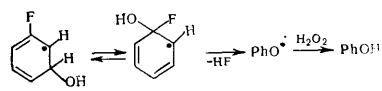
The acid-catalysed fragmentation of cyclohexadienyl radicals is a general phenomenon. Investigation of the reactions of anisole, acetanilide, fluorobenzene, and certain substituted phenols in the Ti^{3+}–H_2O_2 system showed that the adduct of HO· and phenol is recorded by e.s.r. only at pH > 1: in more acid media this adduct is not recorded, but the spectrum of the phenoxy-radical C_6H_5O· is clearly developed. Cyclohexadienyl radicals corresponding to the other benzene derivatives studied were not recorded at all in acid media[23].

These facts are explained by fragmentation of the radicals in acid media:



This last reaction is confirmed also by the pulse radiolysis of phenol in aqueous solutions[35]: the absorption spectrum of the adduct of HO· with phenol (λ_{max} = 330 nm) and the spectrum of the phenoxy-radical (400 nm) are recorded. At 20°C the adduct decomposes with a rate constant of 5000 s^{-1}, while phenoxyl accumulates at the same rate. The rate of conversion of the adduct into phenoxyl is substantially dependent on the pH and the temperature.

The above fragmentation of cyclohexadienyl radicals explains the formation of phenol when such compounds as fluorobenzene are oxidised by Fenton's reagent[23]:



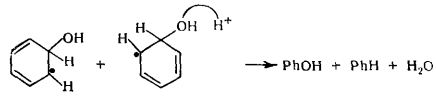
The fact that metal ions (Fe^{2+}, Fe^{3+}, Ti^{3+}) are not responsible for the influence of pH on the composition of the products is proved by results for the hydroxylation of toluene by hydrogen peroxide exposed to ultraviolet radiation[24]. Table 2 shows that the yield of cresols increases with pH, and that this effect is not due to the action of ions.

Table 2.

pH	5.4	3.0	2.0	1.0	0.2
Relative yield of cresols	10	4.2	2.5	0.9	trace

It is interesting that in strongly acidic media the yield of hydroxy-derivatives of anisole is far smaller than the yield of phenol from benzene under the same conditions[24]. The adduct of HO· with benzene is obviously more stable in acid media than is its adduct with anisole. This is confirmed by the clear e.s.r. spectra of C_6H_6O·H in the Ti^{3+} + H_2O_2 system[19], whereas the corresponding adduct of anisole is not recorded by e.s.r.[23]

Variation in pH affects the molar proportions of biphenyl and phenol produced by the ultraviolet irradiation of the C_6H_6 + H_2O_2 system (Table 3).[24] The relative increase in the yield of phenol can be explained by the fact that, in acid media, most of the phenol is formed by disproportionation, which is facilitated by hydrogen ions:



Thus the influence of pH on the composition of the products conforms to the same rules in oxidation by Fenton's reagent and in hydrogen peroxide exposed to ultraviolet radiation.

Table 3.

pH	5.5	3.0	2.0	0.5
[PhPh]/[PhOH]	0.5	0.4	0.23	0.02

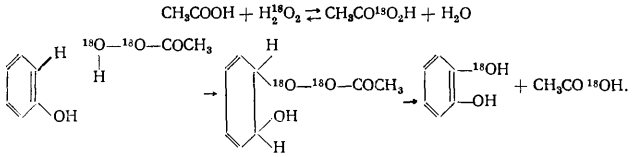
Metal ions (Fe^{3+} and Cu^{2+}) may play an important part in oxidation by Fenton's reagent, since their reactions with organic radicals are well known[36,37]. Additions of Cu^{2+} and F^- ions to Fenton's reagent have been made in the oxidation of anisole, and the effect on the yield of phenols has been examined. The yield is increased by the addition of copper ions, but fluoride ions lower the yield, since they form a stable complex with the Fe^{3+} ions which would have oxidised cyclohexadienyl radicals to phenols.

Important parameters of the species which attacks the benzene ring are the distribution of isomeric products which are formed and the relative reactivities of monosubstituted benzene derivatives and benzene itself towards this species. For example, most monosubstituted benzenes are more reactive than benzene itself towards the phenyl radical, independently of the polar character of the substituent[38]. The sequence of reactivities with Fenton's reagent is[22]

$$PhOCH_3 : PhH : PhCl : PhNO_2 = 6.35 : 1 : 0.55 : 0.14$$

This reactivity series differs from the order for phenylation[38], and indicates that the HO· species is electrophilic. The above reactivity sequence is maintained with hydrogen peroxide exposed to ultraviolet radiation.

The electrophilic nature of the HO· radical is confirmed by the distribution of isomeric phenolic products resulting from the oxidation of substituted benzenes. Table 4 shows that substituents of the first kind orient the group HO· mainly *ortho* and *para*, which is typical of electrophilic substitutions in the benzene series. Not only the HO· radical but also peroxy-acids (peracetic and trifluoroperacetic acids) may act as electrophilic agents[25,26]. Thus the oxidation of phenol by hydrogen peroxide in the presence of acetic acid and $H_2{}^{18}O_2$ yields catechol[25]:



Oxygen is incorporated into the catechol from the oxidant: free hydroxy-radicals are not formed in the reaction.

The action of Fenton's reagent involves attack by the radical HO· as has been noted many times. Several workers have recently obtained e.s.r. spectra of this radical in systems which act similarly to Fenton's

reagent. Table 5 lists the characteristics of the e.s.r. spectra and the conditions under which they have been obtained. It shows that the $Ti^{3+} + H_2O_2$ system generates HO· radicals in concentrations sufficient for detection by this method. The e.s.r. spectrum of the HO· radical differs from that of $HO_2^·$. The $Ce^{4+} + H_2O_2$ system produces solely $HO_2^·$ radicals by the reactions

$$Ce^{4+} + H_2O_2 \rightarrow Ce^{3+} + H^+ + HO_2^·$$
$$Ce^{4+} + HO_2^· \rightarrow Ce^{3+} + H^+ + O_2$$

and is considerably less effective than Fenton's reagent in the hydroxylation of benzene. From this Norman and Smith [18] concluded that $HO_2^·$ radicals are less reactive than HO· towards aromatic systems. However, Coppinger had shown [16] that the $HO_2^·$ radical is able to attack the benzene ring quite effectively.

Table 4. Distribution of isomers in the hydroxylation of substituted benzenes by Fenton's reagent.

Compound	Conditions	Phenols, %			Ref.
		ortho	*meta*	*para*	
Toluene	$Fe^{2+} + H_2O_2$, N_2	55.5	15.0	29.5	24
Toluene	$Fe^{2+} + H_2O_2$, air	71.0	5.0	24.0	18
Anisole	$Fe^{2+} + H_2O_2$, N_2, pH 2.5	81.0	0.5	18.0	24
Anisole	$Cu^{2+} + H_2O_2$	84.0	3.0	13.0	24
Anisole	Fe^{2+}-EDTA + H_2O_2	84.0	—	16.0	22
Anisole	Fe^{2+}-ascorbic acid + H_2O_2	88.0	—	12.0	17
Chlorobenzene	Fe^{2+}-EDTA + H_2O_2	42.0	29.0	29.0	22
Fluorobenzene	Fe^{2+}-EDTA + H_2O_2	37.0	18.0	45.0	22
Nitrobenzene	Fe^{2+}-EDTA + H_2O_2	24.0	30.0	46.0	22
Nitrobenzene	H_2O_2 + ultraviolet	24.0	30.0	46.0	22
Acetanilide	Fe^{2+}-EDTA + H_2O_2	47.0	3.0	50.0	39
Naphthalene	$Fe^{2+} + H_2O_2$	79.2 (1-naphthol)		20.8 (2-naphthol)	21

Table 5. Electron spin resonance spectra of HO· and $HO_2^·$ radicals and their characteristics.

Conditions of recording of spectrum	*g*	ΔH, oersteds	Species	Ref.
1% H_2O_2 soln. + ultraviolet from −70° to +60°C	2.015	1.0	HO·	40
$TiCl_4 + H_2O_2$		1.0	HO·	43
$Ti^{3+} + H_2O_2$, in flow	2.0128	0.7 (28°)	HO· in Ti^{4+} complex	41
	2.0114			
$TiCl_3 + H_2O_2$, rapid mixing at room temp.	2.0117		in Ti^{4+} complex	42
	2.0102			
$Ce(HSO_4)_4 + H_2O_2$, in flow, ice	2.0160	27	$HO_2^·$	44
H_2O_2, β-rays, −187°			HO·	46
$Ti^{3+} + H_2O_2$		1	$HO_2^·$	46
$Ti^{3+} + H_2O_2$ (different ratios)		1.5	HO· and $HO_2^·$ in different ratios	48
$Ti^{3+} + H_2O_2$	2.0115	0.8	$[TiO·OH]^{2+}$	47
	2.0130		$[TiO·O_2H]^{2+}$	45

Many experimental results indicate nevertheless that the principal active species in oxidation by Fenton's reagent is the radical HO·. This is confirmed by the distribution of isomeric phenolic products, by the reactivity sequence of substituted benzenes towards Fenton's reagent, by the similarity with reactions with hydrogen peroxide exposed to ultraviolet radiation, and by the direct recording of the e.s.r. spectra in systems analogous to Fenton's reagent. However, recent e.s.r. studies of such systems as $Ti^{3+} + H_2O_2$ under flow conditions have shown that the e.s.r. signals originate, not from free HO· or $HO_2^·$ radicals but from their complexes with compounds of quadrivalent titanium [45]. It is probable that complexes of this type may also be hydroxylating species, acting as electrophilic agents.

III. MECHANISM OF RADIOLYTIC HYDROXYLATION

Many studies have been made of the hydroxylation of aromatic compounds under the influence of various kinds of radiation—the photochemical oxidation of benzene in aqueous solution on exposure to a mercury lamp [49,50], the oxidation of phenols under the same conditions [51–54], the photolysis of benzene in the gas phase on ultraviolet irradiation [55–59], and the oxidation of benzene and phenol in aqueous solution subject to ultrasonic vibrations [60]—but most of the investigations have used more penetrating, harder radiations—the oxidation of benzene to phenol by the action of neutrons and α-particles [61] and in aqueous solution by the action of X-rays [62–65]. The radiolysis of aromatic compounds in aqueous solution has been effected in many cases by means of cobalt-60 γ-rays [60–101]: studies have been made of the oxidation of benzene [66–92], toluene [93], naphthalene [95], chlorobenzene [97], nitrobenzene [101], anisole [100], *p*-nitrophenol [98] and benzoic acid [99].

In aqueous solution at room temperature, in the absence of oxygen and metal ions, the oxidation of aromatic compounds is effected by products of the radiolysis of water—H_2O_2, HO·, and $HO_2^·$—independently of the type of radiation employed [62,63,68]. The yields of phenols are low, 2.64–2.94 mM kr^{-1}. [67,68] In the presence of oxygen, however, the yield of phenol from benzene increases to G = 2 mol./100 eV. [68] It was first established in 1955 [49,68] that the addition of iron ions (Fe^{2+} or Fe^{3+}) to the aqueous solution increases the yield of phenol, which under certain conditions (oxygen pressure of 10 atm) may reach 6 mol./100 eV. [68] Raising the temperature from 20° to 220°C with the addition of iron ions enables phenol to be obtained from benzene in a yield of 0.035 M with a ratio of water to benzene of 32 : 1. [68] Resins containing both phenolic derivatives and polyphenylenes are formed together with the phenol. After the termination of exposure the reaction develops autocatalytically, and the authors assume that at high temperatures the oxidation of benzene is a branched chain process [68].

Exposure of a solution of benzene to X-rays in the absence of oxygen yields phenol and biphenyl, but in the presence of oxygen hydrogen peroxide and dialdehydes are also obtained [63,64]. Phenol and muconaldehyde are formed in parallel and in equal quantities [64]: G_{ph} = 1.8 and G_{dial} = 1.5.

Before considering the mechanism of the hydroxylation of aromatic compounds in the radiolysis of aqueous solutions, we must discuss the mechanism of the radiolysis of such systems as H_2O–O_2 and H_2O–O_2–Fe^{2+}–Fe^{3+}, since the facts given above make it clear that oxygen and iron ions play a very important part in the oxidation of aromatic compounds in radiolytic systems.

Analysis of the steady states arising in the radiolysis of water and their dependence on various input parameters has shown that the experimental results can be described correctly on the hypothesis that an excited species—an

exciton (ext)—takes part in the radiation-chemical process [102]. In contrast to earlier schemes [103], therefore, the mechanism of the radiolysis of the H_2O–O_2 system involves the reactions [102]

$$H_2O \rightsquigarrow H_2,\ H_2O_2,\ ext,\ H \quad (1)$$
$$ext + O_2 \rightarrow H_3O_3 \quad (2)$$
$$ext + H_2O_2 \rightarrow H_2O + 2HO^{\cdot} \quad (3)$$
$$ext \rightarrow H_2O \quad (4)$$
$$H_3O_3 + H_2O_2 \rightarrow H_2O + O_2 + H_2O_2 \quad (5)$$
$$HO^{\cdot} + H_2O_2 \rightarrow H_2O + HO_2^{\cdot} \quad (6)$$
$$HO^{\cdot} + H_2 \rightarrow H_2O + H \quad (7)$$
$$2HO_2^{\cdot} \rightarrow H_2O_2 + O_2 \quad (8)$$
$$H + O_2 \rightarrow HO_2^{\cdot} \quad (9)$$
$$HO_2^{\cdot} \rightleftarrows H^+ + O_2^- \quad (10)$$
$$O_2^- + H_2O_2 \rightarrow O_2 + HO^{\cdot} + HO^- \quad (11)$$

The above mechanism provides a good quantitative description of the radiolysis of solutions of oxygen at pH 0–6.5. The mechanism of the process at higher pH-values probably differs significantly, owing to the conversion of hydrogen atoms and excitons in alkaline medium into solvated electrons:

$$H + OH^- \rightarrow e_{aq}^- + H_2O \quad (12)$$
$$ext + HO^- \rightarrow e_{aq}^- + HO^{\cdot} \quad (13)$$

A solvated electron is extremely effective in breaking down hydrogen peroxide with formation of the radical-ion O_2^- by the reaction

$$e_{aq}^- + O_2 \rightarrow O_2^- \quad (14)$$

In solutions of Fe^{2+} and Fe^{3+} in sulphuric and perchloric acids saturated with hydrogen and oxygen under pressure the radiation efficiencies of oxidation are extremely high, reaching 100 mol./100 eV under optimum conditions [104,105]. This is evidently due to the chain character of oxidation. The radiolysis of such solutions involves the reactions [102]

$$H_2O \overset{\gamma}{\rightsquigarrow} H,\ \dot{O}H,\ H_2O_2,\ H_2 \quad (0)$$
$$HO^{\cdot} + H_2 \rightarrow H_2O + H \quad (7)$$
$$Fe^{2+} + HO^{\cdot} \rightarrow Fe^{3+} + HO^- \quad (15)$$
$$H + O_2 \rightarrow HO_2^{\cdot} \quad (9)$$
$$Fe^{2+} + HO_2^{\cdot} + H^+ \rightarrow Fe^{3+} + H_2O_2 \quad (16)$$
$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^- + HO^{\cdot} \quad (17)$$
$$Fe^{3+} + H \rightarrow Fe^{2+} + H^+ \quad (18)$$
$$HO_2^{\cdot} \rightleftarrows H^+ + O_2^- \quad (10)$$
$$Fe^{3+} + O_2^- \rightarrow Fe^{2+} + O_2 \quad (19)$$

The cycle formed by reactions (7), (9), (16), and (17) regenerates a certain quantity of HO· radicals, which lays the foundation for development of a chain process. Chain termination takes place by reactions (15), (18), and (19). The conditions for chain propagation are determined by the relation between the reactions involving the growth and the termination of chains. Under certain conditions reaction (16) should be replaced by reaction (8).

Great progress has been made during recent years in the study of radiation processes in aqueous solutions, this being due in considerable measure to the successful application of pulse radiolysis, which permits determination of the absolute rate constants of many reactions involving intermediate products of radiolysis and their characterisation from the absorption spectra recorded during radiolysis [106–112].

When discussing the mechanism of the radiation hydroxylation of aromatic compounds we have repeatedly required a knowledge of the rate constants of the elementary reactions in the radiolysis of aqueous solutions. Rate constants for several primary reactions are therefore listed in Table 6. Thus the radiolysis of water and aqueous solutions involves formation of the radicals HO· and $HO_2^{\cdot}$, which in principle can be hydroxylating agents in the water–aromatic compound system. In the first stage of hydroxylation, as in the action of Fenton's reagent, the HO· radical "adheres" to the benzene ring [29,34,64].

Table 6. Rate constants of elementary reactions in the radiolysis of aqueous solutions (20–25 °C).

Reaction	Rate constant, $M^{-1}\,s^{-1}$	Ref.
$H + O_2$	$(0.53 \div 2.6)\cdot 10^{10}$	113
$H + Fe^{3+}$	$9.0\cdot 10^7$	114
$H + e_{aq}^-$	$2.5\cdot 10^{10}$	115
$HO^{\cdot} + Fe^{2+}$	$2.6\cdot 10^8$	118
$HO_2^{\cdot} + Fe^{3+}$ (0.5 M H_2SO_4)	$7.3\cdot 10^5$	108
$HO_2^{\cdot} + Cu^{2+}$ (pH 2,3)	$1.5\cdot 10^7$	109
$HO_2^{\cdot} + HO_2^{\cdot}$ (pH $\leqslant 3$)	$(1.9 \div 2.7)\cdot 10^8$	111, 116
$O_2^- + O_2^-$ (pH $\geqslant 5$)	$(1.35 \div 1.70)\cdot 10^7$	111
$e_{aq}^- + O_2$	$1.9\cdot 10^{10}$	117
$e_{aq}^- + N_2O$	$9.0\cdot 10^9$	117
$HO^{\cdot} + H_2O_2$	$4.5\cdot 10^7$	118

This reaction has been investigated with many benzene derivatives by pulse radiolysis with recording of the absorption spectra of the cyclohexadienyl radicals [29,34,117–129]. Table 7 gives the spectra of these radicals and the rate constants for reaction between the HO· radical and the aromatic compounds.

Table 7. Rate constants of reaction between HO· and C_6H_5X, and absorption spectra of cyclohexadienyl radicals $C_6H_5X(^{\cdot}OH)$.

Compound	λ_{max}, nm ($HOC_6H_5X^{\cdot}$)	$10^{-9}k_{OH + C_6H_5X}$ at 25 °C, $M^{-1}\,s^{-1}$	Ref.
C_6H_6	313	4.3 ± 0.9	34
		3.3	120, 126
C_6D_6	—	4.7 ± 0.9	34
$C_6H_5NO_2$		1.7	101
		2.0	120
		4.7 ± 0.5	126
C_6H_5COOH	350	2.1	120, 128
	347	4.3 ± 0.8	124
$C_6H_5COO^-$	328		129
C_6H_5Cl	324	4.2	34, 120
C_6H_5Br	326		34
$C_6H_5CH_3$	317	3.0	34, 120
$C_6H_5OCH_3$	—	3.6	120
$C_6H_5NH_2$	—	5.3	120
HOC_6H_4OH	320	12.0	122
C_6H_5OH	320	5.1	34, 120
» pH 7.4	—	14.03	121
» pH 6—7		10.6 ± 0.3	121
» pH 9	330	5.1 ± 0.3	35, 121

The reactivities of substituted benzenes towards HO· have been compared under the same conditions as for the reaction of this radical with *p*-nitrosodimethylaniline. The

rate constants $k_{(HO^{\cdot} + C_6H_5X)}$ have been calculated, as well as the ratios

$$\frac{k_{(HO+C_6H_5X)}}{k_{(HO+C_6H_6)}} = \gamma^{120}.$$

A linear dependence of $\lg\gamma$ on σ_p and σ_m has been obtained for deactivating substituents X and a similar dependence of $\lg\gamma$ on σ_p for other substituents X. The coefficient ρ in the Hammett equation has been calculated as 0.41. The correlation of $\lg\gamma$ with the Hammett σ-parameter and the negative value of ρ confirm the electrophilic character of the radical $HO^{\cdot}$. However, a significant defect of this work [120] is the lack of an analysis of the isomeric phenols, so that σ is compared with the total phenol concentrations, not with the quantities of *para*- and *meta*-isomers formed.

In the absence of oxygen and iron ions the cyclohexadienyl radicals are able to react with the hydrocarbon C_6H_5X and with themselves. In the presence of oxygen and iron ions the radicals are consumed also by reactions with these additions. In acid media the unimolecular conversion of HOC_6H_5X into phenoxyl is also possible [121,122]:

$$HOC_6H_5X \xrightarrow{H^+} C_6H_5O^{\cdot} + H_2X^+$$

The mechanisms of the disproportionation of cyclohexadienyl radicals of type (I), their reaction with hydrocarbons, and also the unimolecular transformation of the radicals in acid media have been discussed in sufficient detail in Section II, and particular features of radiolytic systems have no significant influence on the mechanisms of the above processes.

The pulse radiolysis method has enabled the rates of disproportionation of radicals (I) and of their reaction with oxygen to be measured under identical conditions, and the effect of substituents X on these rates to be established [125]. The values of these rate constants in Table 8 have been used to correlate the quantities

$$\alpha = \frac{k_{(HO^{\cdot}C_6H_5X+O_2)}}{k_{(HO^{\cdot}C_6H_5+O_2)}} \quad \beta = \frac{k_{(2HO^{\cdot}C_6H_5X)}}{k_{(2HO^{\cdot}C_6H_5)}}$$

with the Hammett σ-parameters for the *meta*- and *para*-positions. Good linearity was obtained, and the coefficients in the Hammett equation were calculated as $\rho_\alpha = -1.0$ and $\rho_\beta = -0.75$. [125] Thus electron-donor substituents X tend to increase the rate of reaction of the radicals with molecular oxygen and with one another, whereas electron-acceptor substituents retard these reactions.

In the absence of oxygen a radical of type (I) may be oxidised to phenol by radicals ($HO^{\cdot}$, $HO_2^{\cdot}$) or by Fe^{3+} (Cu^{2+}) ions:

$$I + HO^{\cdot} \rightarrow XC_6H_4OH + H_2O \quad (20)$$

$$I + Fe^{+3} \rightarrow XC_6H_4OH + Fe^{2+} + H^+ \quad (21)$$

The rate constant of reaction (21) has been estimated as $k_{Fe^{3+} + HO^{\cdot}C_6H_6} = 7000\ M^{-1}\ s^{-1}$ at room temperature on the basis of the kinetic scheme set up for the oxidation of benzene in aqueous solutions in the presence of Fe^{2+} ions (0.001 M) on exposure to γ-rays. [76] The occurrence of reaction (21) is confirmed by a study of the effect of the concentration of potassium hexacyanoferrate(III) on the yield of hydroxybenzoic acids in the radiation hydroxylation of benzoic acid in aqueous solution in the presence of nitrous oxide [99]

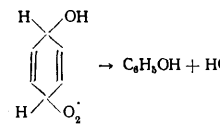
$$(HOC_6H_5COOH)^{\cdot} + Fe(CN)_6^{3-} \rightarrow HOC_6H_4COOH + Fe(CN)_6^{4-} + H^+.$$

The rate constant (7000) of reaction (21) is much smaller than that of the reaction between the radical (I) and molecular oxygen (Table 8): i.e. addition of oxygen to the radical (I) is more rapid than the transfer of an electron by reaction (21).

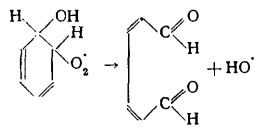
Table 8. Effect of substituent X on rate of reaction of cyclohexadienyl radicals $HO^{\cdot}C_6H_5X$ (I) with oxygen and with each other.

X	$10^{-6}k_{I+O_2}$, $M^{-1}s^{-1}$	$10^{-8}k_{I+I}$, $M^{-1}s^{-1}$	E_{I+I}, kcal mole^{-1}
NO_2	2.5	5.0	6.0
CN	2.9	3.9	4.7
COC_6H_5	3.7	3.66	4.7
$COCH_3$	3.82	4.20	4.3
SO_2NH_2	4.2	3.68	5.1
COOH	5.25	3.95	4.3
I	7.0	4.0	5.0
Cl	7.95	4.86	3.5
Br	9.6	4.2	3.9
OH	4.9	11.0	6.7
OCH_3	16.4	5.73	5.8
NH_2	25.4	16.0	3.9
H	400	4.55	3.5
CH_3	390	3.85	3.0
C_2H_5	555	4.2	3.6

A radical of type (II) ($HO.C_6H_5.XO_2^{\cdot}$) differs from cyclohexadienyl radicals (I) in absorbing at shorter wavelengths [34]. Such radicals are able to decompose by the unimolecular reactions (22) and (23) to form phenol and dialdehydes respectively [78,79]:

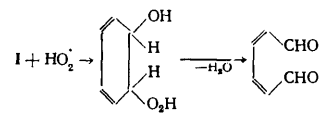


$$\rightarrow C_6H_5OH + HO_2^{\cdot} \quad (22)$$



(23)

Reaction (23) was first proposed by Kartasheva and Pikaev [78]. These workers have since shown that, in the radiolysis of benzene in aqueous solution containing iron ions and oxygen, the ratio $k_{22}/k_{23} = 1.4$. Muconaldehyde can be formed not only by reaction (23) but also by the reaction



(24)

Kartasheva and Pikaev [80] consider that, in the oxidation of benzene, the radical (II) may be involved in the reaction

$$O_2^{\cdot}C_6H_6OH + Fe^{2+} + H^+ \rightarrow HOOC_6H_6OH + Fe^{3+} \quad (25)$$

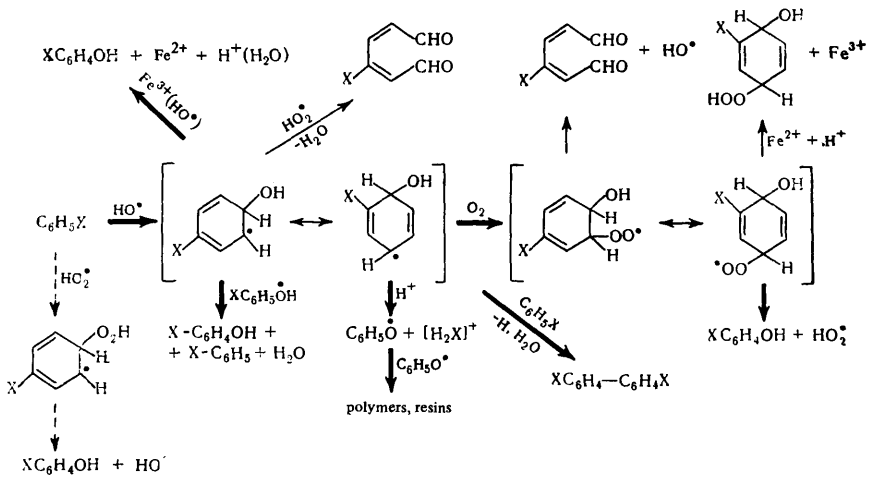
They give the ratios $k_{25}/k_{22} = 6300\ M^{-1}$ and also $k_{25}/k_{23} = 9000\ M^{-1}$: i.e. with 0.001 M Fe^{2+} the rate of reaction (25) will exceed those of reactions (22) and (23) by factors of 6 and 9 respectively. The hydroperoxide formed by reaction (25) may react in two ways:

$$HOOC_6H_6OH \rightarrow HO^{\cdot} + \dot{O}C_6H_6OH \quad (26)$$

$$HOOC_6H_6OH + Fe^{2+} \rightarrow Fe^{3+} + HO^- + \dot{O}C_6H_6OH \quad (27)$$

According to these workers [80] $k_{27}/k_{26} = 5900\ M^{-1}$.

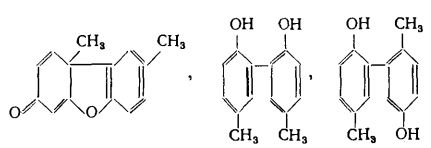
Scheme 1



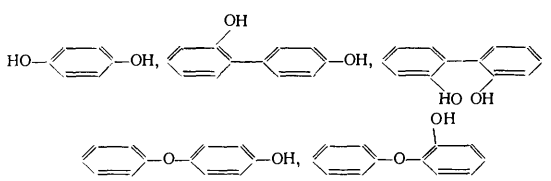
Every possible reaction in the radiation-chemical hydroxylation of benzene and its derivatives is shown in Scheme 1. Reliably demonstrated reactions of molecules and radicals are indicated by thick arrows; reactions which have been introduced into kinetic schemes, and are characterised by the constants of relatively reliably demonstrated processes, are denoted by ordinary arrows; and finally hypothetical reactions [75] are indicated by broken arrows.

Let us consider in greater detail the formation and reactions of phenoxy-radicals. As already noted [35], in acid media the adduct of the radical HO· with phenol is converted to phenoxyl with the elimination of water. The radicals $HOC_6H_4O^{\cdot}$ and $^{-}OC_6H_4O^{\cdot}$ (λ_{max} = 415 and 425 nm respectively) are recorded in the pulse radiolysis of quinol; they are formed from the adduct of HO· and quinol with a rate constant of $(4.6–8.8) \times 10^4$ s^{-1}. [122]

Phenoxy-radicals interact with one another. At 20°C the radicals $HOC_6H_4O^{\cdot}$ react with a rate constant of 1.09×10^9 M^{-1} s^{-1} to form quinone and quinol (disproportionation); [122] and tolyloxy-radicals $CH_3C_6H_4O^{\cdot}$ dimerise with a rate constant of 6.5×10^9 M^{-1} s^{-1}. [119] The recombination of tolyloxy-radicals has been proved [52] to yield dimers of the three types



The compounds



have been detected among the products of the photolysis of phenol [54].

It is very important to examine the effect of the reaction conditions—presence or absence of oxygen, addition of nitrous oxide, etc.—on the distribution of phenolic isomers in the radiation-chemical oxidation of substituted benzenes. Table 9 gives the distribution of isomeric phenols formed by the γ-irradiation of dilute aqueous solutions of benzoic acid, nitrobenzene, and anisole, and includes for comparison the distribution of isomers resulting from the hydroxylation of these compounds by Fenton's reagent.

Table 9. Distribution of isomeric phenols on γ-irradiation of dilute aqueous solutions of substituted benzenes at room temperature.

Compound	Conditions	Isomers			Ref.
		ortho	*meta*	*para*	
C_6H_5COOH	N_2O, $K_3Fe(CN)_6$	29	12	59	99
$C_6H_5NO_2$	air	50	31	19	101
$C_6H_5NO_2$	0.02 M N_2O	40	21	39	101
$C_6H_5NO_2$	0.014 M N_2O + 0.00023 M O_2, Fenton's reagent	51	31	18	110
$C_6H_5NO_2$	0.00023 M O_2	24	30	46	22
$C_6H_5OCH_3$	0.02 M N_2O	37	0	63	100
$C_6H_5OCH_3$	Fenton's reagent	80	0	20	100
$C_6H_5OCH_3$		81	1	18	24

Table 9 shows that the distribution of isomers varies with the conditions of hydroxylation: the distribution obtained on exposure in an atmosphere of nitrous oxide coincides with that obtained with Fenton's reagent, since the same species—the HO· radical—is the hydroxylating agent in this case. In the presence of nitrous oxide the reaction

$$e_{aq}^{-} + N_2O \rightarrow HO^{-} + N_2 + HO^{\cdot}$$

takes place with $k = 9 \times 10^9$ M^{-1} s^{-1} (Table 6). In an atmosphere of oxygen or air the reaction

$$e_{aq}^{-} + O_2 \rightarrow O_2^{-} \xrightarrow{H^+} HO_2^{\cdot}$$

occurs with $k = 1.9 \times 10^{10}$ M^{-1} s^{-1} (Table 6), and in my view the main hydroxylating species is now the $HO_2^{\cdot}$ radical, which produces a change in the distribution of isomers. Both radicals—HO· and $HO_2^{\cdot}$—operate in the presence of nitrous oxide and oxygen, since the reactions of the solvated electron with oxygen and with nitrous oxide are competitive. The hydroxylation of naphthalene at 55 to 120°C (on γ-irradiation) yields a little 2-naphthol (7–10%) at low temperatures, but with rise in temperature the

quantity increases to 75% (at 170°C), which is evidently due to a change in the relative proportions of HO· and $HO_2^·$ radicals with rise in temperature [95]. Thus the distribution of phenolic isomers in radiation hydroxylation indicates that two radicals—HO· and $HO_2^·$—may be active species.

The radiation oxidation of benzene and toluene in the presence of iron and copper ions at 100–200°C is especially interesting [84–94]. Iron(II) sulphate ensures a high yield of phenol (2.5% on the initial benzene) both with and without irradiation. On catalysis by the Fe^{3+} ion phenol is formed in considerable quantities only above 180°C. When copper(II) sulphate is used the yield of phenol is equally high (up to 3.7% on the initial benzene) with and without irradiation. Iron and copper chlorides are less active catalysts than are the sulphates [86,87]. The quantity of phenol formed is greatly diminished by addition of the anions Cl^- and SO_4^{2-}, but increasing the concentration of copper(II) sulphate from 0.0001 M to 0.01 M at 198°C increases the yield of phenol. Although phenol is the main reaction product, small quantities ($\sim 10^{-4}$ M) of such compounds as benzene diols, maleic, acetic, and formic acids, acetone, and acetaldehyde are also formed [90]. The oxidation of toluene under similar conditions (1 ml of toluene in 15 ml of an aqueous solution of an iron or a copper salt under 30 atm of oxygen at 100 to 200°C) yields $(2.5–4.0) \times 10^{-4}$ M benzaldehyde, $(0.2–2.1) \times 10^{-5}$ M benzyl alcohol, $\sim 0.5 \times 10^{-5}$ M benzoic acid, and up to 0.4×10^{-5} M cresols [93].

Study of oxygen transfer by means of ^{18}O showed that oxygen is incorporated into phenol both from water and from the gas phase [91]. Isotopic analysis of the phenol formed from an equimolecular mixture of benzene and hexadeuterobenzene gave $k_H/k_D = 1.2$. The small isotope effect suggests that detachment of a hydrogen atom from benzene occurs to a slight extent in the limiting step. On the basis of experimental results and published data Japanese investigators have suggested a mechanism for the oxidation of benzene and toluene, transferring without reservation to higher temperatures (180–200°C) a scheme adopted for radiation oxidation at room temperature. At high temperatures the reaction

$$HO^·C_6H_5X + O_2 \rightarrow HOC_6H_5XO_2^· \rightarrow HOC_6H_4X + HO_2^·$$

is most probably able to occur in a single step without formation of a peroxy-radical of type (II). Iron and copper ions act at high temperatures as initiators of oxidation, since they generate radicals by the reactions

$$Fe^{2+} + O_2 \rightarrow Fe^{3+} + O_2^- \xrightarrow{H^+} HO_2^· \quad (28)$$

$$Fe^{3+} + H_2O \rightarrow Fe^{2+} + H^+ + HO^· \quad (29)$$

The possible occurrence of reaction (29) has been shown by several workers [130,131]. Japanese authors attribute to iron ions also the role of stabilisers of peroxy-radicals (II), but even the existence of these radicals at high temperatures is doubtful.

The inhibiting action of chloride ions is explained by the reaction

$$Cl^- + HO^· \rightarrow Cl^· + HO^- \quad (30)$$

the rate constant of which is 1.8×10^8 M^{-1} s^{-1} at pH 2 and 25°C, increasing in 0.8 *N* sulphuric acid by a factor of 8. [118] The rate constant for the reaction between the radical HO· and benzene is 4.3×10^9 M^{-1} s^{-1}, and if the temperature variation of this constant is assumed to be the same as that of k_{30}, the reactions of HO· with benzene and with the chloride ion may compete with one another at high temperatures.

Japanese authors consider the oxidation of benzene and toluene to be a branched chain process. On the basis of published results [132] they suggest the scheme of branching

$$PhO^· + PhH \rightarrow PhOH + Ph^· \quad (31)$$
$$Ph^· + O_2 \rightarrow PhO_2^·$$
$$PhO_2^· + PhH \rightarrow PhOOH + Ph^·$$
$$PhO_2H + Fe^{3+} \rightarrow PhO_2^· + Fe^{2+} + H^+$$
$$PhO_2H + Fe^{2+} \rightarrow PhO^· + Fe^{3+} + HO^-$$
$$PhO_2H \rightarrow PhO^· + HO^·$$

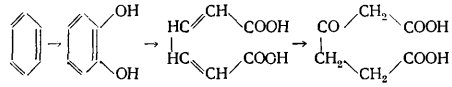
There are several grave objections to this scheme. Reaction (31) cannot occur at an appreciable rate, since the $C_6H_5O^·$ radical is relatively inactive, while the carbon–hydrogen bond in benzene is stable. This reaction is endothermic (17 kcal $mole^{-1}$) and is unable to compete successfully with such reactions of the phenoxy-radical as oxidation or addition to benzene. The hydroperoxide C_6H_5OOH does not exist as a molecular compound (especially at high temperatures), and therefore all reactions involving it are irrelevant. The mechanism of the acceleration of the oxidation of benzene in the presence of iron and copper ions will be considered in detail in Section IV dealing with the catalytic oxidation of aromatic compounds.

With regard to the part played by iron (copper) ions in radiation hydroxylation in aqueous solution, the addition of iron ions at room temperature ensures that a certain quantity of the hydroxylating agent (HO· radicals) is regenerated (reactions 16 and 17). The oxidised form of the ion (Fe^{3+} or Cu^{2+}) oxidises radicals of type (I) to phenol. At high temperatures the metal ions also initiate oxidation, since they generate HO· and $HO_2^·$ radicals by reaction with oxygen. At high concentrations of Fe^{2+} ions inhibition of the oxidation of benzene may become possible, since $k_{Fe^{2+} + HO^·} = 2.6 \times 10^8$ (Table 6), while other results indicate that $k_{HO^· + C_6H_6}/k_{HO^· + Fe^{2+}} = 3.2$ at 25°C. [133,134]

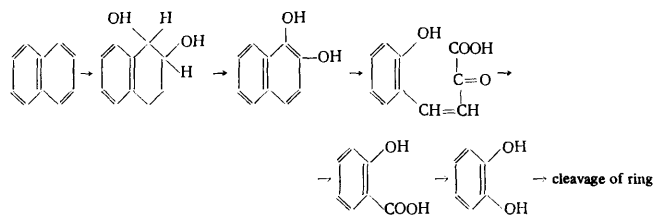
IV. CATALYTIC HYDROXYLATION

A. Enzymatic Hydroxylation of Aromatic Compounds

As already noted, micro-organisms are able to assimilate aromatic compounds, converting them into *o*- and *p*-benzenediols and then cleaving the ring to give aliphatic acids [3,135]. The oxidation of benzene yields catechol, and phenol and *cis-cis*-muconic acid accumulate [136]. Benzene oxidase has been extracted from cells grown on benzene, which it transforms according to the scheme [137]



Cultures of five different micro-organisms break down naphthalene as follows [138]:



A detailed account of the mechanism of the microbiological oxidation of aromatic and heterocyclic compounds has been published [139], but the first, most decisive stage of oxidation—hydroxylation of the aromatic ring—is not entirely understood. This stage usually involves active catalysis by enzymes, which transfer oxygen to the reaction product. Table 10 gives some examples of the hydroxylation of aromatic compounds by means of enzymes.

Table 10.

Substrate	Enzyme	Reaction product	Ref.
Salicylic acid	peroxidase + dihydroxyfumaric acid	2,4-dihydroxybenzoic acid	146
Phenylalanine	tyrosinase	tyrosine	146
3,4-Xylenol	tyrosinase	4,5-dimethylcatechol	142

In the above cases oxygen is incorporated into the hydroxy-group from molecular oxygen—not from water or hydrogen peroxide [140,142]—and the new hydroxy-group enters the *ortho*-position relative to orienting substituents of the first kind in the benzene ring. The oxygen molecule is a weak oxidant, since oxidation must involve rupture of the strong bond between the oxygen atoms, which are bound to one another by one two-electron bond and two three-electron bonds [sic]. The addition of two electrons to the oxygen molecule, as occurs on reduction to O_2^{2-} or H_2O_2, weakens the bond between the oxygen atoms. This function of reductants for the oxygen molecule is performed by metal ions, which are inevitably present in redox enzymes (Table 11). [143]

Table 11.

Metal-containing enzyme	No. of metal ions per enzyme mol.
Peroxidase	1 Fe
Tyrosinase	3-4 Cu
Catalase	4 Fe
Cytochrome oxidase	2 Fe + 2 Cu

The activation of molecular oxygen is not the only function of metal ions [144]: they may also stabilise structures, initiate chain processes, form catalytic units having qualitatively new catalytic functions, etc.

We shall consider below mechanisms of the activation of molecular oxygen and the schemes of the hydroxylation of aromatic systems which are known for peroxidases and tyrosinase [141]. Iron(II) and copper(I) ions allow the O–O bond to be ruptured by a mechanism involving reduction of the first pair of electrons. The ferrous ion combines with oxygen to form a perferryl ion FeO_2^{2+}, in which the bond between the oxygen atoms is less stable than in molecular oxygen, since electrons pass from iron to the oxygen.

Evidence of the existence of an intermediate perferryl ion has been obtained in work [144–148] on the kinetics of the oxidation of Fe^{2+} by oxygen, which is represented by the equations

$$Fe^{2+} + O_2 \rightleftarrows FeO_2^{2+}$$

$$FeO_2^{2+} + Fe^{2+} + H_2O \rightarrow Fe^{3+}OOH + Fe^{2+}OH$$

The bond in the perferryl ion may be broken with the formation of a ferryl ion FeO^{2+}. Bray and Gorin [149], from kinetic data for the reaction

$$2Fe^{3+} + H_2O_2 \rightleftarrows Fe^{2+} + FeO^{2+} + H_2O$$

suggested the existence of this ion in inorganic reactions.

There is evidence that FeO^{2+} or a similar ion of the same degree of oxidation may be present in biological systems [150]. The $FeOOH^{2+}$ ion, like the $FeOH^{2+}$ ion, is well known in inorganic chemistry from its charge-transfer spectra in solutions containing H_2O_2 and Fe^{3+}. Thus enzymes may contain iron ions of different degrees of oxidation:

$FeOOH^{2+}$ or $FeOH^{2+}$ (iron 5) – complex I,
FeO^{2+} (iron 4) – complex II,
FeO_2^{2+} – complex III,

Chance [151] showed that catalase reacts with hydrogen peroxide to form the complex (I), which reacts further with hydrogen peroxide to form molecular oxygen and water. One-electron reduction of the complex (I) yields the ferryl ion (complex II):

$$FeOOH^{2+} + H^+ + e \rightarrow FeO^{2+} + H_2O.$$

In the case of peroxidases complex (I) acts as a one-electron oxidant, the most probable mechanism being

$$Fe^{3+} + H_2O_2 \rightarrow FeOOH^{2+} + H^+$$

$$FeOOH^{2+} \xrightarrow[-H_2O]{H} FeO^{2+}$$

$$FeO^{2+} + PhH \rightarrow PhOFe^+ + H^+$$

$$PhOFe^+ + H^+ \rightarrow PhOH + Fe^{2+}$$

The hydroxylating species is the ferryl ion (complex II).

Copper is able to form complexes analogous to complexes (I)–(III) of iron-containing enzymes. It is present in tyrosinase as the univalent ion [152]; direct reaction of molecular oxygen yields the percupryl ion CuO_2^+, the analogue of complex (III) in iron-containing enzymes. The percupryl ion is then reduced to the complex (II) (the cupryl ion), which hydroxylates the benzene ring by transferring one of the atoms of the oxygen molecule to the substrate. Such a process is typical of enzymes which have been termed "oxidases of mixed function". [153] The mechanism of the action of tyrosinase is represented by the scheme [141]

$$Cu^+ + O_2 \rightleftarrows CuO_2^+ \quad \text{or} \quad Cu^+O_2Cu^+$$

$$CuO_2^+ + 2e + 2H^+ \rightarrow CuO^+ + H_2O$$

$$CuO^+ + PhH \rightarrow PhOCu^+ + H^+$$

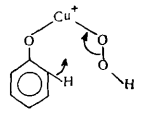
$$PhOCu^+ + H^+ \rightarrow PhOH + Cu^+$$

Evidence of the existence of the cupryl ion in tyrosinase has been obtained from the denaturation of the enzyme by acid and from kinetic investigations [154].

B. Models of Hydroxylase Biocatalysts and the Mechanism of Their Action

The detailed mechanism of the action of hydroxylases can be elucidated by means of models. Konecny, Havinga, and others [155–159] studied models of complex (I). Hydrogen

peroxide and the cupric ion hydroxylate benzene and sodium benzoate to phenol and salicylic acid respectively [155]. Studies have been made [156–159] of the copper-catalysed hydroxylation of phenols and aniline in the presence of amines. This model resembles tyrosinase: both the model and tyrosinase contain copper and hydroxylate in the *ortho*-position. A mechanism was proposed [156] in which the oxidant was hydrogen peroxide formed by the successive oxidation of certain reaction products. The Cu^{2+} ion, phenol, and the peroxide form the complex (I), which directs hydroxylation to the *ortho*-position. The Cu^{2+} ion is acting here as an acid catalyst, polarising the O–O bond so that it is cleaved with the formation of ions, the pair of electrons remaining on the oxygen near the copper atom. The action of the copper ion in this reaction resembles that of the two protons in acid-catalysed oxidations by hydrogen peroxide [160]. Complex (I) containing copper



like the iron-containing complex (I), may take part in free-radical reactions. It was suggested [156] that the hydroxylating agent in the copper–amine–phenol system was the OH^+ ion, formed by the breakdown of complex (I) and acting as an electrophilic agent. It will be shown below that this is incorrect.

Oxidative coupling of phenols is possible in the presence of amine–copper catalysts, e.g. [161]

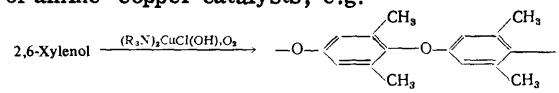


Table 12 gives the results of a study of models of peroxidases which hydroxylate aromatic compounds [162–165].

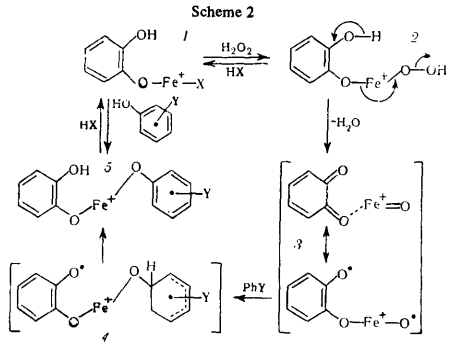
Table 12. Hydroxylation by systems (Fe^{3+}–H_2O_2–benzenediol) simulating peroxidases.

System	Substrate	Distribution of phenols			Ref.
		ortho	*meta*	*para*	
Fe^{3+} — H_2O_2 — Catechol	anisole	64	3	33	162
Catechol	nitrobenzene	48	26	26	164
Catechol	chlorobenzene	45	15	40	164
Fe^{3+} — H_2O_2 — Quinol	anisole	65	5	35	162

From a comparison of the resulting distribution of isomeric phenols with that obtained by the action of Fenton's reagent (Table 4) and a detailed kinetic investigation of hydroxylation involving the Fe^{3+}–H_2O_2–catechol system [163,164] it can be confidently stated that neither the radical HO· nor the radical $HO_2^·$ is the hydroxylating species in this case: hydroxylation occurs by the mechanism of Scheme 2. [164]

In this mechanism the overall rate of the process is limited by the formation of complexes *2* and *3*. The latter complex is a hybrid of all possible states of the metal, which explains its stability. It reacts as a radical, giving a distribution of isomeric phenols which is typical of radical attack on an aromatic ring. The ligands used to make complex *3* capable of hydroxylation were catechol, quinol, 3,4-dihydroxybenzoic acid, 3-methoxycatechol, etc. Phenol, ascorbic acid, and benzoquinone exhibit less catalytic activity or none at all, owing to the instability of the complex *3* when the above ligands are used. The interaction of form *3* with organic solvents involving removal of a hydrogen atom explains the inhibiting effect of the latter on hydroxylation.

Scheme 2



The relation between the above system and the action of such enzymes as peroxidase and catalase is that, according to George [166,167], the oxygen atom is bound to iron in the same way in these enzymes as in form *3*. In peroxidase and catalase this form is evidently stabilised by porphyrins having redox characteristics closely similar to those of catechol.

Table 13. Hydroxylation by systems (containing molecular oxygen) simulating oxidases.

System containing O_2	Substrate	Distribution of phenols, %			Ref.
		ortho	*meta*	*para*	
Fe^{2+} + EDTA + ascorbic acid	anisole	43	18	39	17
Fe^{2+} + 2,4,5-triamino-6-hydroxypyrimidine	anisole	49	13	38	169
$TiCl_3$	acetanilide	35	32	33	171
Sn^{2+}/HPO_4^{2-}	acetanilide	36	35	29	33
Fe^{2+} + 2-mercaptobenzoic acid	acetanilide	57	3	40	175
Fe^{2+} + 2-mercaptobenzoic acid	toluene	61	13	26	175
Microsome + NADP	toluene	59	13	28	175

Several enzymes (tyrosinase, etc.) act as "mixed-function oxidases", [153] which are characterised by the transfer of an oxygen atom from molecular oxygen to a substrate RH in conformity with the equation [168]

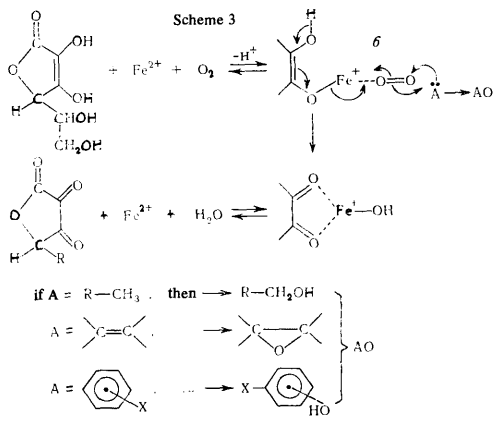
$$RH + DH_2 + O_2 \rightarrow ROH + D + H_2O$$

where DH_2 is a hydrogen donor. Such oxidases hydroxylate aromatic compounds to phenols, oxidise aliphatic compounds to alcohols, and epoxidise ethylenic compounds, which immediately excludes the radical HO· as a possible agent in their action. Several systems have been investigated which might be regarded as models of mixed-function oxidases [17,39,169–175]. These models help to answer the questions how molecular oxygen is activated,

how electrons are transferred to the oxygen molecule, and how this transfer is connected with hydroxylation of the substrate [176]. We shall first consider results (summarised in Table 13) for the hydroxylation of aromatic compounds by molecular oxygen in which such model systems are involved.

Table 13 shows that, for several substrates, the distribution of isomeric phenols differs from that for hydroxylation by Fenton's reagent (Table 4): i.e. the radical HO· is not in this case the hydroxylating species. Several papers have shown that hydrogen peroxide is not an intermediate product which might be formed and be responsible for hydroxylation [39,167,174]. Hence a special mechanism of hydroxylation is applicable to these models. The hydroxylating species in the O_2–$TiCl_3$–acetanilide system was assumed [171] to be the $HO_2^{\cdot}$ radical, which is less electrophilic than HO·, and will therefore give a distribution of isomeric phenols characteristic of nuclear attack by radicals. However, with other systems (e.g. O_2–Sn^{2+}–HPO_4^{2-}), which not only hydroxylate aromatic compounds but also oxidise aliphatic compounds, the $HO_2^{\cdot}$ radical cannot be accepted as the attacking species. Therefore several workers [39,170,174] suggest a mechanism consisting essentially in the reduction of molecular oxygen by metal ions to a so called "oxenoid" capable of transferring an oxygen atom to the substrate mostly by an electrophilic mechanism. According to Hamilton [170] the model of a mixed-function oxidase (Fe^{2+} + O_2 + ascorbic acid) acts by the mechanism of Scheme 3.

Scheme 3



According to Scheme 3 the oxidising agent is the complex *6*, where the function of the iron ion is to combine with the reducing agent and oxygen, transmitting electrons to the latter in the transition state. The iron ion enables a singlet oxygen atom to be transferred from the bound oxygen molecule to the substrate in such a way that intermediate diradicals are unnecessary. If a triplet oxygen atom were transferred, the process would be less advantageous energetically owing to the formation of a triplet reaction product, which would be less stable than a singlet product. Simultaneous transfer of the proton of ascorbic acid to the complex with molecular oxygen and transfer of electrons by means of the iron ion probably occur in complex *6*, leading to oxidation of the complex ascorbate and reduction and stabilisation of the oxygen atom not transferred to the substrate. But the other oxygen atom, having six electrons (hence analogous to carbenes CR_2 and nitrenes NR, which also have six electrons around the carbon or nitrogen and are very reactive), is incorporated into the substrate. This way a four-electron exchange is accomplished with minimum movement of nuclei.

There are in general two principal ways in which "oxene" :Ö: can act as an oxidant: (1) four-electron reduction of molecular oxygen and two-electron oxidation of the substrate take place in a single step:

$$DH_2 \cdot A \cdot O_2 \rightarrow D \cdot AO \cdot H_2O$$

(2) the same act can occur in two steps:

$$DH_2 \cdot A \cdot O_2 \rightarrow DO \cdot A \cdot H_2O$$
$$DO \cdot A \cdot H_2O \rightarrow D \cdot AO \cdot H_2O$$

In these schemes DH_2 represents the reduced form either of the enzyme or of the coenzyme, and AO the product of reaction between the substrate A and oxygen. Study of model systems shows [170] that both mechanisms are possible.

C. Mechanism of the Oxidation of Benzene to Phenol catalysed by Iron and Copper Ions in Aqueous Solution at 180–220°C

Studies of oxidation in the presence of copper and iron ions in aqueous solution have been made on the conversion of benzene into phenol at 180–220°C, [177–183] of phenol into catechol and quinol at 110°C, [184] and of ethylbenzene [185]. However, a detailed investigation of the kinetics and the mechanism of such catalysed oxidation has been made only on benzene [177–183]. Oxygen at 35–50 atm was used to oxidise benzene dissolved in water. In the absence of copper and iron ions no oxidation is observed in aqueous solution at 180–200°C, but in the presence of these ions benzene is oxidised to phenol, whose accumulation is clearly autocatalytic in character [177–187]. Phenol is an intermediate product in the reaction, which is proved by experiments in which phenol is introduced into the initial oxidising mixture. Resins and small quantities of compounds of low-molecular weight—acetone, acetaldehyde, acetic acid, etc.—are formed from phenol.

The introduction of small quantities of phenol into the initial mixture accelerates the oxidation of benzene in aqueous solution, whereas in hydrocarbon media phenol inhibits oxidation. It has been shown convincingly [180] that the phenol undergoing oxidation is responsible for the autocatalysis in the accumulation of phenol from benzene.

The valency state of the iron ions changes during the reaction: if Fe^{3+} ions are introduced into the initial aqueous solution of benzene, Fe^{2+} ions appear during the reaction; and conversely. All kinetic rules are very similar for catalysis by copper and by iron ions [177,178]: with increase in the benzene concentration the maximum reaction velocity passes through a maximum, while the maximum phenol concentration increases linearly. With increase in the catalyst concentration W_{max} passes through a maximum, while the maximum phenol concentration increases in the case of copper ions. The reaction velocity decreases with increase in the hydrogen-ion concentration. Under optimum conditions the yield of phenol is 57% based on the benzene consumed.

The mechanism of the oxidation of benzene is closely connected with that of the oxidation of phenol and the valency changes undergone by the catalytic ions. A detailed study was therefore made [181] of the mechanism of

the oxidation of phenol by oxygen catalysed by iron ions. This showed that the simultaneous occurrence of three modes of oxidation of phenol—by Fe^{3+} ions, by molecular oxygen, and by free radicals—in sulphuric acid solution at 200°C. The following mechanism was proposed for the oxidation of phenol in the presence of iron ions in aqueous solution:

$$PhOH + O_2 \rightarrow PhO^{\cdot} + HO_2^{\cdot} \qquad (0')$$

$$PhOH \overset{K_0}{\rightleftarrows} PhO^- + H_3O^+$$

$$PhO^- + O_2 \rightarrow PhO^{\cdot} + O_2^- \qquad (0'')$$

$$PhO^- + Fe^{3+} \rightarrow PhO^{\cdot} + Fe^{2+} \qquad (1')$$

Free radicals are formed in the oxidation of Fe^{2+} ions by the reactions [145–148,186,187]

$$Fe^{2+} + O_2 \rightarrow Fe^{3+} + O_2^- \qquad (2')$$

$$Fe^{2+}\,aq \overset{K_0}{\rightleftarrows} FeOH^+ + H^+$$

$$FeOH^+ + O_2 \rightarrow FeOH^{2+} + O_2^- \qquad (2'')$$

$$H^+ + O_2^- \rightarrow HO_2^{\cdot}$$

$$HO_2^{\cdot} + Fe^{2+} \rightarrow HO_2^- + Fe^{3+}$$

$$HO_2^- + H^+ \rightleftarrows H_2O_2$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\cdot} + HO^-$$

The resulting radicals $HO^{\cdot}$ and $HO_2^{\cdot}$, which are indistinguishable kinetically and will henceforward be denoted by $r^{\cdot}$, react with Fe^{2+} and phenol:

$$Fe^{2+} + HO^{\cdot} \rightarrow Fe^{3+} + OH^- \qquad (3)$$

$$PhOH + r^{\cdot} \rightarrow PhO^{\cdot} + rH \qquad (4)$$

The resulting phenoxy-radicals either recombine or are oxidised to products [52,54,119,122].

Comparison of the above scheme with experiment showed that the rate of oxidation of Fe^{2+} by oxygen was

$$4\,[Fe^{2+}]\,[O_2]\,(k_{2'} + k_{2''}K_2[H^+]^{-1}),$$

and the overall rate of oxidation of phenol

$$W = (2k_0[O_2] + k_1[Fe^{3+}] + k_4[r^{\cdot}])[PhOH]_0,$$

where

$$k_0 = k_{0'} + k_{0''}K_0[H^+]^{-1}, \quad k_1 = k_{1'}[H^+]^{-1}.$$

Experimental results obtained at 200°C were used to determine the values of $k_{0'}$, $k_{0''}K_0$, $k_{2'} + k_{2''}K_2$, and $k_{1'}$, and to estimate the proportions of the three reactions in the total consumption of phenol.

Benzene when present reacts with the radicals $HO^{\cdot}$ and $HO_2^{\cdot}$ to form phenol:

$$C_6H_6 + HO^{\cdot} \xrightarrow{O_2} PhOH + HO_2^{\cdot}$$

$$C_6H_6 + HO_2^{\cdot} \rightarrow PhOH + HO^{\cdot}$$

The relative part played by each radical in the hydroxylation of benzene cannot be determined from the experimental results. However, it is clear that the catalytic oxidation of benzene in aqueous solution at 180–220°C is a coupled autocatalytic radical-ion oxidation of benzene and phenol involving short chains (4–6 steps). This conclusion was reached after a detailed study of the mechanism of oxidation of the phenol formed from benzene and an estimate of the contributions of the different reactions to the total formation of radicals in the system [182,183]. This estimate showed that, in the initial stages of the process, iron (or copper) ions act as initiators for the oxidation of benzene, forming radicals by reaction with oxygen (2′ and 2″). When the process has developed, the oxidation of phenol by oxygen (reactions 0′ and 0″) begins to play the main part in the generation of free radicals. Thus the role of accelerator of the reaction passes to phenol, while the metal ions may merely promote conversion of the radical $HO_2^{\cdot}$ into $HO^{\cdot}$.

V. HYDROXYLATION OF AROMATIC COMPOUNDS ON OXIDATION TOGETHER WITH ALCOHOLS AND HYDROCARBONS

The oxidation of hydrocarbons involves the accumulation of peroxides, which decompose with the formation of radicals. It may therefore be expected that aromatic compounds will undergo hydroxylation in the presence of easily oxidisable hydrocarbons and alcohols. Emanuel' and Denisov [188,189] were the first to demonstrate the fundamental possibility of oxidising liquid benzene to phenol under pressure at temperatures below the critical point (288°C), and discovered that such additives as cyclohexane and cyclohexanone (2 vol.%) could initiate the oxidation of benzene. The introduction of these compounds, which undergo oxidation by a chain mechanism, accelerates significantly the accumulation of phenol from benzene, but the oxidation of benzene remains self-inhibiting and cannot be conducted to high degrees of conversion.

Considerable rates of accumulation of phenol from benzene can be achieved by increasing the proportion of easily oxidisable substance. Thus when benzene is oxidised together with cyclohexane (10–20 mole %) in air (60 atm) at 220–250°C the rate of accumulation of phenol is $\sim 10^{-5}$ M s^{-1}. [190–192]. A kinetic study of the combined oxidation of benzene with cyclohexane, cyclohexanol, and cyclohexanone showed that autocatalysis in the oxidation of benzene was due to the autocatalytic oxidation of the additives [190–192]. In this case the developed reaction comprises the combined oxidation of cyclohexane and cyclohexanone and of benzene and phenol. The reaction remains self-inhibiting, owing to the inhibiting effects of benzene and of the resins formed from phenol. Other additives—methyl- and ethyl-cyclohexane, toluene, and *p*-xylene—may also exert an inhibiting action. Attempts to stimulate the oxidation of benzene by readily oxidisable organic additives have been undertaken also in the catalysed oxidation of benzene in aqueous solution [179]: the oxidation in aqueous copper(II) sulphate solution (0.125 M) at an oxygen pressure of 35 atm and 180°C is accelerated by the addition of cyclohexane and cyclohexanone (2 vol.% based on the benzene), whereas similar additions of cyclohexanol, propan-2-ol, cumene, and cyclohexene lengthen the induction period in the formation of phenol from benzene. Japanese workers [193] have made a systematic investigation of the simultaneous oxidation of benzene and toluene with the addition of ethylbenzene, cumene, cyclohexane, cyclohexene, n-hexane, t-butyl alcohol, propan-2-ol, and ethanol in solutions of iron(II) sulphate under 30 atm of oxygen at 180°C. They established that small additions of all the compounds diminish the yield of phenol from benzene and of benzaldehyde from toluene, but the yield of these products is increased by increasing the proportion by volume of the additives.

In all the above investigations the simultaneous oxidation of benzene and the additives was accompanied by hydroxylation of the benzene. However, several workers have found [194–196] that the addition of aromatic compounds diminishes the rate of oxidation of the other component, and phenolic products are not observed. Phenol is formed by the combined oxidation of benzene and a readily oxidisable additive only at sufficiently high temperatures—at 180–200°C in aqueous solution and at 220–250°C in

organic media. At lower temperatures phenol is not formed, and benzene either behaves as an inhibitor of oxidation [196] or simply changes the dielectric properties of the medium [197].

The kinetics and the mechanism of the hydroxylation of aromatic compounds have been studied when oxidised together with alcohols [198–204]. The combined oxidation of benzene and of the phenol formed from it by oxygen in aqueous solution has been established at 180–240°C; [198] a detailed study of the kinetics of the process showed that phenol was directly involved in the oxidation of benzene. To establish the character of the oxidation of benzene to phenol in aqueous solution it is important to compare the rates of oxidation of the two compounds under similar conditions. For this purpose the oxidation of benzene at 200°C was investigated on a sample which had initially been primed with phenol at its kinetically equilibrium concentration under these conditions. The rate of consumption of phenol was then equal to its rate of formation so long as there was no significant decrease in the benzene concentration. The rate of oxidation of benzene was 4.5×10^{-5} M s^{-1}, whereas the rate of oxidation of phenol at the kinetically equilibrium concentration but in the complete absence of benzene was 1.9×10^{-5} M s^{-1} under otherwise similar conditions. Thus the rate of oxidation of benzene is more than double that of phenol under analogous conditions, which indicates that the oxidation of benzene is a chain reaction. A detailed kinetic investigation of the oxidation of phenol by oxygen in phosphoric-acid solution (pH 1.55) supported the reaction mechanism [197,200]

$$\mathrm{PhOH} + \mathrm{O_2} \rightarrow \mathrm{PhO^{\cdot}} + \mathrm{HO_2^{\cdot}} \qquad (0')$$

$$\mathrm{PhOH} \rightleftarrows \mathrm{PhO^-} + \mathrm{H^+}$$

$$\mathrm{PhO^-} + \mathrm{O_2} \rightarrow \mathrm{PhO^{\cdot}} + \mathrm{O_2^-} \qquad (0'')$$

$$\mathrm{O_2^-} + \mathrm{H^+} \rightleftarrows \mathrm{HO_2^{\cdot}}$$

$$\mathrm{PhOH} + \mathrm{HO_2^{\cdot}} \rightarrow \mathrm{PhO^{\cdot}} + \mathrm{H_2O_2} \qquad (1)$$

$$\mathrm{PhOH} + \mathrm{H_2O_2} \rightarrow \mathrm{PhO^{\cdot}} + \mathrm{H_2O} + \mathrm{HO^{\cdot}} \qquad (2)$$

$$\mathrm{PhOH} + \mathrm{HO^{\cdot}} \rightarrow \mathrm{PhO^{\cdot}} + \mathrm{H_2O} \qquad (3)$$

$$\mathrm{PhO^{\cdot}} + \mathrm{PhO^{\cdot}} \rightarrow \mathrm{Products}\ .$$

Comparison of this scheme with the experimental relations enabled the rate constants of reactions (0′), (0″), and (2) to be evaluated as (in $M^{-1} s^{-1}$) $k_{0'} = 4.9 \times 10^8 \exp(-25\,600/RT)$, $k_{0''} = 3.5 \times 10^{12} \exp(-17\,000/RT)$, and $k_2 = 7.3 \times 10^{10} \exp(-23\,700/RT)$. The phenoxide ion reacts with oxygen at 200°C with a rate constant exceeding the rate constant of reaction (0′) by a factor of 10^7, but in acid media the two reactions occur at comparable rates, since the concentration of phenoxide ions is very small. The oxidation of phenol by oxygen is accompanied by the formation of $HO_2^{\cdot}$ radicals and hydrogen peroxide, which then reacts with the phenol. The rate constants of reactions (0′) and (2) can be used to calculate kinetically the equilibrium concentrations of hydrogen peroxide, and compare the results with the experimental values. Such a comparison has been made at 157° and 180°C, and shows good agreement between experimental and calculated quantities of hydrogen peroxide, which supports the above mechanism.

The radicals $OH^{\cdot}$ and $OH_2^{\cdot}$, formed by the oxidation of phenol, hydroxylate benzene. Whereas the hydroxylating power of the former radical is well known, the similar part played by $HO_2^{\cdot}$ in the combined oxidation of aliphatic alcohols and aromatic compounds has been demonstrated quite recently [201–204]. For this purpose benzene was introduced into two systems—comprising hydrogen peroxide and an initiator together with water and with methanol and molecular oxygen—in which $HO_2^{\cdot}$ radicals are generated continuously but no $HO^{\cdot}$ radicals are formed [201]. Under these conditions $HO_2^{\cdot}$ is formed by the reaction of initiator radicals and peroxy-radicals of methanol $RO_2^{\cdot}$ with hydrogen peroxide. Evidence has been obtained [205,206] of the rapid exchange $R^1OO^{\cdot} + R^2OOH \rightarrow R^1OOH + R^2OO^{\cdot}$. The radicals $RO_2^{\cdot}$ in the oxidisable alcohol exchanged for $HO_2^{\cdot}$ in the hydrogen peroxide formed, the degree of this substitution depending on the ratio of the rate constants $k_{RO_2^{\cdot} + H_2O_2}/k_{HO_2^{\cdot} + RH}$. At 30°C, for example, 0.11 to 0.47 M ROOH is sufficient for complete exchange of peroxy-radicals with the hydroperoxide during oxidation of the hydrocarbon [207]. It is therefore most likely that at 110–220°C there will be complete exchange of peroxy-radicals with hydrogen peroxide taken in the same concentrations, for the H–O bonds to be broken have almost the same strength in the hydroperoxides as in hydrogen peroxide.

In the presence of an initiator and hydrogen peroxide, phenol is formed from benzene both in water (in an atmosphere of argon) and in oxidisable methanol (in oxygen). Phenol is formed only by the reaction of benzene with free radicals: in the absence of an initiator hydrogen peroxide does not hydroxylate benzene under the experimental conditions, since no appreciable decomposition of the peroxide with the formation of $HO^{\cdot}$ radicals takes place. Therefore the formation of phenol from benzene in the systems—H_2O–H_2O_2—initiator and CH_3OH–H_2O_2–initiator–O_2—must be regarded as proof of hydroxylation by the radical $HO_2^{\cdot}$. Kinetic study of the combined initiated oxidation of methanol and benzene showed that the initial rate of accumulation of phenol $W_0^{C_6H_5OH}$ is directly proportional to the square root of the initial concentration of the initiator: i.e. it increases linearly with the concentration of free radicals in the system. Three types of free radicals—those from the initiator, $\diagdown\!\!\diagup C(OH)OO^{\cdot}$, and $HO_2^{\cdot}$—are present in the oxidisable alcohol (the concentration of $\diagdown\!\!\diagup C(OH)^{\cdot}$ radicals is very small in the presence of molecular oxygen and they can be ignored). Experiments in water showed that in the presence of hydrogen peroxide an initiator does not ensure the hydroxylation of benzene: i.e. the initiator radicals are not involved in hydroxylation. In methanol undergoing oxidation, therefore, benzene can be hydroxylated by $\diagdown\!\!\diagup C(OH)OO^{\cdot}$ and $HO_2^{\cdot}$ radicals. Experiments in methanol with different initial concentrations of hydrogen peroxide showed that this factor has hardly any effect on $W_0^{C_6H_5OH}$: i.e. benzene is hydroxylated either by both peroxy-radicals or by $HO_2^{\cdot}$ alone. The hydroxylation of benzene in the H_2O–H_2O_2–initiator system, in which $\diagdown\!\!\diagup C(OH)OO^{\cdot}$ radicals are in general absent, again proves that $HO_2^{\cdot}$ is able to hydroxylate benzene. Thus the hydroxylating power of the $HO_2^{\cdot}$ radical has been demonstrated.

The oxidation of alcohols involves the formation of hydrogen peroxide, which may yield $HO_2^{\cdot}$ radicals by reaction with the peroxy-radicals of the alcohol. Hydroxylation of benzene can therefore be expected when it is oxidised in the presence of alcohols. In fact phenol is formed in all cases of such oxidation in air at 50 atm and 200°C. [202,204] Its rate of accumulation shows a well defined autocatalytic character.

In order to obtain quantitative parameters a study was made of the initiated oxidation of mixtures of alcohols and benzene at 145°C. Measurements were made of the initial rates of accumulation of phenol $W_0^{C_6H_5OH}$ and of

the total oxidation products of the alcohol W_0^{alc}. The initial stages of oxidation of an alcohol mixed with the benzene were shown [201] to be described by the equation for chain reactions with quadratic termination:

$$W_0^{alc} = (k_2/\sqrt{k_6})_{alc}[R-OH]_0\sqrt{W_i},$$

where $[ROH]_0$ is the initial alcohol concentration, k_2 the rate constant of chain growth, k_6 the termination rate constant, and W_i the rate of initiation. The oxidation of benzene was characterised by the parameter $(k_2/k_6^{1/2})_b$, calculated by means of the equation

$$W_0^{PhOH} = (k_2/\sqrt{k_6})_b[C_6H_6]_0\sqrt{W_i}.$$

Table 14. Initiated oxidation of benzene–alcohol mixtures in air at 50 atm and 145°C in the presence of 0.054 M t-butyl peroxide ($W_i = 1.18 \times 10^{-5}$ M s^{-1}).

Alcohol	M	Benzene, M	$10^4 W_0^{alc}$, M s^{-1}	$10^3(k_2/k_6^{1/2})_{alc}$	$10^6 W_0^{C_6H_5OH}$, M s^{-1}	$10^{-4}(k_2/k_6^{1/2})_b$	No. of steps
Propan-2-ol	9.15	3.35	5.80	18.4	3.84	3.32	49
Ethanol	13.7	2.25	1.80	3.80	1.70	2.20	15
Methanol	19.7	2.25	1.82	2.70	0.47	0.61	15
t-Butyl alcohol	8.5	2.25	0.16		0.10		1—2

Experimental results for the initiated oxidation of mixtures of benzene and alcohols are given in Table 14, from which it follows that the rate of accumulation of phenol is a maximum for the initiated oxidation of benzene in propan-2-ol.

The oxidation of mixtures of propan-2-ol and benzene or toluene has been studied at 110–150°C. Rates of initiation were calculated for various temperatures by means of the equation $W_i = k_i[TBP]_0$, where TBP represents t-butyl peroxide and $k_i = 4.4 \times 10^{14}\exp(-35\,000/RT)$ s^{-1}. [207, 208] The initial rates of accumulation of phenol, benzaldehyde + benzyl alcohol, cresols, and acetone were used to calculate the rate constant ratios $k_2/k_6^{1/2}$ for benzene, toluene at the methyl group, cresols, and propan-2-ol: for a toluene–propan-2-ol mixture

$$(k_2/\sqrt{k_6})_{i\text{-PrOH}} = 1.30 \cdot 10^4 \exp(-11000/RT),$$
$$(k_2/\sqrt{k_6})\ \text{at}\ CH_3 = 3.20 \cdot 10^2 \exp(-9600)/RT),$$
$$(k_2/\sqrt{k_6})_{\text{cresols}} = 17.8\exp(-9100/RT),\ M^{-1/2}\,s^{-1/2}.$$

and for a benzene–propan-2-ol mixture

$$(k_2/\sqrt{k_6})_{i\text{-PrOH}} = 2.40 \cdot 10^3 \exp(-9800/RT),$$
$$(k_2/\sqrt{k_6})_b = 4.25 \cdot 10^2 \exp(-11700/RT),\ M^{-1/2}\,s^{-1/2}.$$

The hydroxylation of monosubstituted benzene derivatives in the course of the initiated oxidation of propan-2-ol has been studied at 137°C in air at 50 atm. The experimental results are listed in Table 15.

The mechanism of the oxidation of alcohols has now been thoroughly investigated [209]. The primary oxidation products are hydroperoxides, which break down into hydrogen peroxide, and carbonyl-containing compounds—acetone, formaldehyde, and acetaldehyde from propan-2-ol, methanol, and ethanol respectively. Hydrogen peroxide accumulates in considerable concentrations in the oxidation of secondary and primary alcohols, the quantity depending on the nature of the alcohol. In fact, in benzene–alcohol mixtures with the same conditions of initiation at 145°C, the quantity of hydrogen peroxide and its rate of accumulation increase in the sequence—methanol < < ethanol < propan-2-ol. Peroxy-radicals react with hydrogen peroxide to form hydroperoxy-radicals. Thus $HO_2^\cdot$ radicals are formed in mixtures of alcohols with benzene and its derivatives as a consequence of a series of reactions such as

$$\text{Initiator} \xrightarrow{k_i} r^\cdot \xrightarrow{RH} rH + R^\cdot \qquad ROOH \rightarrow H_2O_2 + \text{>C=O}$$
$$R^\cdot + O_2 \rightarrow RO_2^\cdot \qquad RO_2^\cdot + H_2O_2 \rightarrow HO_2^\cdot + ROOH$$
$$RO_2^\cdot + RH \rightarrow ROOH + R^\cdot \qquad HO_2^\cdot + RH \rightarrow H_2O_2 + R^\cdot \text{ etc.}$$

These radicals hydroxylate the aromatic compounds and react with one another:

$$XC_6H_5 + HO_2^\cdot \rightarrow XC_6H_4OH + HO^\cdot \qquad 2\,HO_2^\cdot \rightarrow H_2O_2 + O_2.$$

Table 15. Initiated oxidation of propan-2-ol (70 ml) mixed with monosubstituted benzenes (30 ml) at 137°C in the presence of 0.108 M di-t-butyl peroxide.

C_6H_5X	$[C_6H_5X]_0$, M	Length of chain	$10^2(k_2/k_6^{1/2})_{alc}$	$10^4(k_2/k_6^{1/2})_{ar}$	$10^4(k_2/k_6^{1/2})_{ar}$	
					ortho	*m + p*
C_6H_6	3.36	50	1.44	2.51	—	—
$C_6H_5CH_3$	2.82	53	2.09	2.24	1.12	1.12
C_6H_5Cl	3.11	64	2.14	3.43	1.48	1.94
$C_6H_5NO_2$	2.94	12	0.39	0.83	0.42	0.41
C_6H_5OH	0.50	3	0.11	—	—	—

At later stages the $HO_2^\cdot$ radicals react with the phenols which are formed, and both the latter and the resins which accumulate from them tend to inhibit oxidation [202].

The concentration of $HO_2^\cdot$ radicals in alcohol–benzene mixtures is $(\alpha W_i/k_6)^{1/2}$, where α represents the completeness of exchange of $RO_2^\cdot$ for $HO_2^\cdot$ radicals. Thus with the same initiation the concentration depends on α and k_6. The constant k_6 is greatly influenced by the medium [197], and α by the ease of oxidation of the alcohol. The combined effect of these factors is that the $HO_2^\cdot$ concentration, and hence the rate of hydroxylation of aromatic compounds $W = k_2^{ar}[XC_6H_5]_0[HO_2^\cdot]$, increase in the sequence—methanol < ethanol < propan-2-ol—corresponding to the ease of oxidation of the alcohols. Table 15 show that, in propan-2-ol undergoing oxidation, all monosubstituted benzenes are hydroxylated with formation of the corresponding phenols. The isomeric distribution of the resulting substituted phenols differs substantially from that obtained on hydroxylation by Fenton's reagent (Table 16). This indicates that in the present systems the benzene ring is attacked not by the $HO^\cdot$ radical, as with Fenton's reagent, but by another species—the $HO_2^\cdot$ radical.

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A detailed examination of the mechanisms of the hydroxylation of aromatic compounds shows that various species can act as hydroxylating agents depending on the conditions—the $HO^\cdot$ radical (Fenton's reagent and radiolytic systems), the $HO_2^\cdot$ radical (catalytic conversion of benzene into phenol at high temperatures, the combined oxidation of aromatic compounds together with alcohols and hydrocarbons, and also perhaps in radiolysis at high temperatures), and complexes of iron-containing enzymes with oxygen. In many papers different mechanisms are

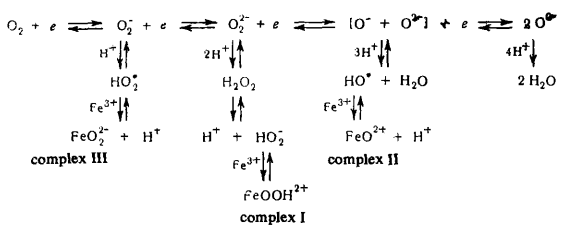
often sharply contrasted with one another; however, we shall attempt to show the relation between them by systematically examining the reduction of an oxygen molecule and the fate of the resulting intermediate species in the presence of ions of variable valency, e.g. iron. Scheme 4 shows the stepwise reduction of an oxygen molecule and the formation of every possible hydroxylating species.

Table 16. Distribution of isomers in the hydroxylation of benzene derivatives in propan-2-ol undergoing oxidation and by means of Fenton's reagent.

XC_6H_5	Combined oxidation of benzene and propan-2-ol			Fenton's reagent			Ref.
	ortho	*meta*	*para*	*ortho*	*meta*	*para*	
$C_6H_5CH_3$	50	25	25	55.5	15.0	29.5	24
		meta—para					
C_6H_5Cl	43	57		42	29	29	22
$C_6H_5NO_2$	51	49		24	30	46	22

According to George [167] the oxidising power of oxygen varies with the stage at which oxidation terminates. If molecular oxygen is reduced to the superoxide anion, and the latter is unable to react further, oxygen is a weak oxidising agent. A higher degree of oxidation is achieved when the superoxide ion combines with a proton to form $HO_2^{\cdot}$. In the reduction of hydrogen peroxide oxygen behaves as an oxidant of medium strength, approximately the same as Fe^{3+}. [176] In the presence of Fe^{3+} ions (or Ti^{4+}, etc.) $HO^{\cdot}$ and $HO_2^{\cdot}$ radicals are able to form complexes with the metals, and thus become stabilised. The ferryl ion FeO^{2+} can be regarded as an $HO^{\cdot}$ radical stabilised by the Fe^{3+} ion. Scheme 4 shows the possible hydroxylating agents and their modes of interconversion.

Scheme 4



A very important aspect of the hydroxylation of aromatic compounds is the nature of the attack on the ring. Although the $HO^{\cdot}$ radical attacks the ring by an electrophilic mechanism, as indicated by the distribution of isomers produced by Fenton's reagent and in radiolytic systems, the $HO_2^{\cdot}$ radical will give a distribution of isomers which is more typical of radical substitution in the benzene ring. Very contradictory results are obtained for the distribution of isomeric hydroxylation products with model systems of mixed-function peroxidases and oxidases and with the enzymes themselves. However, this discrepancy can be eliminated when it is remembered that the agents which attack the benzene ring in these cases are able to react in different forms—as radicals and as ions of different signs. Hamilton considers [170] that the character of the attack on the benzene ring, and hence the distribution of isomers, may change with model systems from radical to electrophilic and even to nucleophilic. It all depends on which state—ionic or radical—predominates with the given hydroxylating species. This state depends on the type of metal and especially on the ligand surrounding it. For example, hydroxylation by means of Fe^{2+}–mercaptobenzoic acid–O_2 yields a distribution of isomers which is characteristic of electrophilic reactions; the same distribution of isomers is obtained by the hydroxylation of toluene in the toluene–t-butyl hydroperoxide–$AlCl_3$ system [210], in which the benzene ring is attacked by the t-butyloxonium cation $[(CH_3)_3COH_2]^+$ by a definitely electrophilic mechanism. However, replacement of the ligand in the Fe^{2+}–EDTA–ascorbic acid–O_2 system produces a sharp change in the distribution of isomers, since the nature of the attacking species changes. There are in general many forms of the attacking complex in the latter case, so that it is necessary to consider the state of the complex as a whole and to know which form is the most significant, for this form will determine the character of the attack on the benzene ring.

We note in conclusion that the study of hydroxylation mechanisms is especially valuable in biochemistry, since reactions of this type occur widely in biological systems. Work during recent years has shown that the mechanism of free oxidations, which play a part in temperature control and several specific metabolic functions, such as the formation of metabolites by oxidation, the detoxication of poisonous compounds, etc., consists in hydroxylation of the substrate [211]. The most widespread is hydroxylation accomplished by a special respiratory chain comprising enzymes of free [non-phosphorylating] oxidation. This system is present in liver microsomes, where foreign compounds and several natural metabolites are converted into non-toxic polar products, the initial stage in these transformations being hydroxylation of the molecule.

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Comparison of the Activities of Catalysts for Heterogeneous Catalytic Reactions

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The existing methods for comparing catalytic activities in terms of various parameters of the kinetic equation and the Arrhenius equation are discussed. A criterion is proposed for estimating the reliability of the results obtained by these methods. The conditions for and limits of their applicability have been defined.
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1. REACTION RATE AS A MEASURE OF CATALYTIC ACTIVITY

Despite its wide employment in studies on catalysis, the term "catalytic activity" is exceptionally indeterminate, since various kinetic parameters are used, and not always justifiably, as a measure of activity. In some reports it is actually not stated at all what is meant by this term. To accord with the significance of the phenomenon of catalysis, the change in the rate of chemical reaction as the result of the introduction of the catalyst into the system should be adopted as a measure of catalytic activity[1]. Since the rate of the non-catalysed process is usually negligibly small compared with the catalysed rate, the rate of reaction in the presence of the catalyst may be regarded as an accurate measure of activity[1-4].

We shall define the rate of a heterogeneous catalytic reaction as a change in the number of reactant or product molecules per unit time per unit catalyst surface. On the basis of this definition, we shall examine the expressions for the rate of reaction in reactors with stationary catalyst beds. Under steady-state conditions in an ideal-mixing flow reactor (a gradient-free reactor, in particular a stirred flow reactor), the rate of reaction is constant both with respect to time and over the entire catalyst surface. If the amount of substance i changes by ΔN_i moles in a stream of reaction mixture passing through a catalyst bed with a surface area S during a time t, the rate of reaction is

$$v = \pm \frac{\Delta N_i}{St}, \qquad (1)$$

where the sign depends on whether the substance i is formed or consumed. When the rate of reaction is expressed in terms of various components of the reaction mixture, account must be taken of the stoichiometric coefficients. In a static ideal-mixing reactor, the rate of reaction is the same at each instant over the entire surface but varies with time. Therefore the rate at a given time is

$$v = \pm \frac{1}{S}\frac{dN_i}{dt}. \qquad (2)$$

In an ideal plug flow reactor under steady state conditions, the rate of reaction varies along the catalyst bed but remains constant with respect to time for each section of the bed. Therefore for an infinitely thin bed with a surface area dS, at right angles to the axis of the reactor, the rate is

$$v = \pm \frac{1}{t}\frac{dN_i}{dS}. \qquad (3)$$

For a flow reactor, the amount of substance is usually expressed in terms of the number of moles passing through the cross-section of the reactor per unit time: $N' = N/t$. Then Eqn. (3) becomes[5,6]

$$v = \pm \frac{dN_i'}{dS}.$$

The rate equations (1)–(3) can be formulated in terms of other variables. For example, for an ideal plug flow reactor,

$$v = \pm \frac{dN_i}{t\,dS} = \frac{N_0}{t}\frac{d\alpha}{dS} = \frac{N_0}{ts\rho}\frac{d\alpha}{dw} = \frac{N_0}{ts\rho\sigma}\frac{d\alpha}{dl}, \qquad (4)$$

where α is the degree of conversion, N_0 is the number of moles of the starting materials supplied to the reactor during a time t, $\pm N_i = N_0 d\alpha$, s and ρ are respectively the specific surface and the bulk density of the catalyst, σ is the cross-sectional area, and dl and dw are the length and the volume of a catalyst bed with a surface area dS. If the contact time $\tau = w/u$ is employed as a variable for a reaction without a change in the number of molecules, w being the volume of the catalyst bed and u the volume of gas passing through the cross-section of the bed per unit time, Eqn. (4) becomes

$$v = \frac{N_0}{ts\rho}\frac{d\alpha}{dw} = \frac{N_0}{ts\rho u}\frac{d\alpha}{d\tau} = \frac{P_0}{RTs\rho}\frac{d\alpha}{d\tau}, \qquad (5)$$

where $N_0/t = P_0 u/RT$ and P_0 is a constant pressure of the starting material at the inlet to the reactor. An analogous expression for the rate of reaction in terms of the contact time may be written for an ideal-mixing flow reactor:

$$v = \pm \frac{\Delta N_i}{tS} = \frac{N_0\alpha}{ts\rho w} = \frac{P_0}{RTs\rho}\frac{\alpha}{\tau}. \qquad (6)$$

In a reaction involving a change in the number of molecules, the flow rate u becomes a function of the degree of

conversion and the contact time τ in the flow reactor is determined by highly complex formulae, which depend on the form of kinetic equation[7]. Here one can employ as a variable in the rate equation[8] the quantity $\tau' = w/u_0$, where u_0 is the volume of gas passing into the reactor per unit time.

Our definition of the rate of reaction is not unique. Apart from the area of the catalyst surface[5,6,9,10], the rate of reaction may be referred to its unit weight[11], unit volume[12,13], or the length of the bed[14]. It is also possible to refer the rate to the surface area of the active phase or to the number of its active centres if these quantities are known†. The above definitions involve the number of moles of the substance in the numerator and can be readily interconverted on multiplication by appropriate constants. The definition of the rate of reaction in terms of the concentration of the substance[15-17] instead of its amount is not universal and is applicable only to reactions at constant volume, when the concentration varies only due to the reaction and not due to a change in the volume of the system system[10,18,19].

By definition, the rate of reaction v is the rate per unit catalyst surface. However, in the literature the rate of reaction is usually defined as the quantity v' calculated from the experimental data (the observed rate), which refers to a catalyst with a surface area S and the rate of reaction $v = v'/S$ is called the specific rate. We may note that the possible heterogeneity of the surface does not preclude the assignment of the observed rate v' to unit surface, since v characterises the average activity of 1 m^2 of the surface area of the given catalyst. Although in the vast majority of cases the observed rate of reaction on solid catalysts is proportional to their amount[20], it is useful to verify this experimentally. Such a test[21-24] confirms the validity of the definition of the activity of catalysts, since, if the experimental conditions are chosen erroneously, the above proportionality may not in fact obtain. For example, it will not hold for very long contact times in a flow reactor, when a linear relation is obtained between the yield of products per unit time and the rate of supply of the starting material, as has in fact been observed[25,26]. In this case the yield corresponds to equilibrium[27] and is attained on part of the catalyst bed, while the remainder is inactive.

In this review we shall not consider the experimental methods for the determination of the rate of reaction. The problem of the choice of experimental conditions to ensure that the observed rate of reaction characterises the activity of the catalyst has been most fully examined by Boreskov[1,20,28] and also by Dowden and Bridger[29], Germain[3], and de Mourgues[30]. The rate of reaction must be measured under isothermal conditions with the catalyst surface in a steady state and in the absence of an effect of heat and mass transfer processes, i.e. in the kinetic region‡. For a reversible reaction, the rate of the process in one direction only must serve as a measure of activity and not the observed rate, which is equal to the difference between the rates in the forward and reverse directions.

The rate of reaction in the presence of a given catalyst depends on temperature and the concentrations (or pressures) of the reactants and products and also extraneous substances. By virtue of this dependence, the rates for different catalysts can be compared only at the same temperature and pressure and for the same composition of the reaction mixture. Despite this, one sometimes encounters in the literature comparisons where the relevant mixture composition is not stated[31]. The relative activities of a series of catalysts found for the same composition of the reaction mixture may be altered for a different composition owing to varying forms of the kinetic equations valid for these catalysts.

In a gradient-free reactor the rate of reaction is calculated from data for a single experiment by Eqn. (6). It is more difficult to satisfy the conditions of a constant composition of the reaction mixture. It is incorrect to compare the rates of reaction for the same composition and rate of supply of the mixture of starting materials as is sometimes done[32-34]. This is because under such standard conditions the mixture compositions in the system differ owing to the different activities of the catalysts. Identical compositions of the reaction mixture can be achieved by varying the degree of conversion, the rate of supply of the starting materials, the composition of the mixture of starting materials supplied, or the amount of the catalyst as was done by Dzis'ko and coworkers[35-37]. It is also possible to find the kinetic equation for each catalyst and to use it to calculate the rate of reaction for a particular composition of the reaction mixture[38].

In integral reactors it is impossible to measure the rate of reaction but it can be found by the graphical differentiation of the kinetic curve. It can also be calculated from the differential kinetic equation by substituting specified concentrations of the reactants and the rate constant obtained by verifying the integral equation[39]. When the reaction is carried out in an "adsorption layer"[22,31,40,41], the condition of a constant composition of reaction mixture must be replaced by the condition of identical surface concentrations.

A special case of the comparison of catalysts in terms of the rate of reaction for a constant composition of the reaction mixture is the comparison based on the "initial rate", i.e. the rate at the start of the reaction when the concentration of reaction products is zero. Naturally, the concentrations of starting materials in such a comparison must be the same. The initial section of the "degree of conversion–time" (duration of contact) kinetic curve can never be measured directly and therefore the initial rate can only be found by extrapolation. The minimum degree of conversion determined experimentally depends on the accuracy of the analytical method and other conditions. The extrapolation is performed on the assumption that near the zero time the same kinetic law holds as in the region of conversions accessible to experiment.

The method of initial rates is usually employed when the experimental curve has a linear section which on extension passes through the origin of coordinates[24,30,42-45]. A linear section, i.e. a constant reaction rate, is characteristic of the initial part of the kinetic curve described by equations of the Langmuir–Hinshelwood type or by power functions without product inhibition, which in the region of low conversions can be approximated by the equation for zero-order kinetics[46]. Evidently the wider is the region

† The assignment of the rate of reaction to unit surface may be purely formal if the entire surface is not active, which sometimes happens for a catalyst with a large surface area or when the surface area of the active phase of the catalyst is unknown. In some cases the very concept of the catalyst surface is without significance (zeolites). We have adopted the definition of the reaction rate which is most widely used in the Russian literature.

‡ For industrial processes in the diffusion region, a quantitative comparison of the activities of catalysts is impossible; one can only compare the yields of products under specified conditions.

under which a constant reaction rate is observed under these conditions (up to 50% [44] and 60% [45] conversion), the lower is the accuracy needed to demonstrate it. If the accuracy of the analysis does not allow the attainment of the region which may be linear, the use of a tangent to the curve, as in the work of Wade et al.[47], involves large errors. When the reaction kinetics at moderate conversions permit the assumption of a linear section, interpolation formulae and in particular Newton's formula [48,49] may be recommended for extrapolation of the curve.

The application of the method of initial rates to reactions inhibited by products is open to objection (Kiperman [50] and Boudart [51]), since the kinetic equation $v = kC_i^n/C_j^m$, where C_i and C_j are respectively the concentrations of the reactant and the product, is not converted into the equation for zero-order kinetics in the region of low conversions [46]. The slope of the curve described by this equation is infinite at $t = 0$ and extrapolation of the curve is pointless.

There exists the opposite view [52,53] that the initial rate may be determined independently of the form of the kinetic equation, since a power function with inhibition cannot describe the region of low conversions where reaction products are virtually absent. Indeed the rate of reaction in the initial instant cannot be infinite. However, as already stated, a linear section must be always obtained to determine the initial rate. Without this, the absence of product inhibition cannot be assumed, since sometimes it already has an appreciable influence for conversions not exceeding 1% [51].

A flow reactor with a small amount of catalyst, which allows experiments at low conversions and which is called a differential reactor [54-56], is frequently used to determine the initial rate. As in a stirred flow reactor, the rate is calculated by Eqn. (6), i.e. the slight changes in the rate in a thin catalyst bed are neglected. As stated above, the constancy of the rate at low conversions depends not only on the type of reactor and the experimental conditions but also on the type of kinetic equation. Nevertheless, sometimes this problem is not discussed and only the maximum degree of conversion is reported [57]. In determinations of the rate of reaction at moderate and high product concentrations with the aid of the differential reactor [23,56,58,59], the type of kinetic equation does not play any role. In this region the determination of the rate does not involve an extrapolation.

2. COMPARISON OF CATALYST ACTIVITIES IN TERMS OF THE REACTION RATE CONSTANT

We shall formulate in a general form the dependence of the reaction rate on temperature and the concentrations of the reaction mixture components:

$$v = f(T, C_i, C_j).$$

As a rule, for heterogeneous catalytic reactions the multiplier $k(T)$, which depends only on temperature but not on pressure or the composition of the reaction mixture, may be taken outside the function f:

$$v = k(T)\varphi(T, C_i, C_j).$$

In particular, this possibility is illustrated by the review [60] of kinetic equations for catalytic gas-phase reactions investigated in flow reactors. By analogy with the kinetics of simple single-stage reactions, the multiplier $k(T)$ can be conventionally [61] referred to as the reaction rate constant.

For simple reactions, the rate constant is the proportionality coefficient between the rate of reaction and a power function of reactant concentrations only. For heterogeneous catalytic processes, the function φ is usually more complex. Fractional and negative power exponents and variation with product concentration and with temperature are typical. The rate constant in equations with several constants (for example in equations of the Langmuir–Hinshelwood type) is not equal to the rate for unit concentrations of the reaction mixture components. Only in single-term power equations can the rate constant for a multistage process be formally treated like the rate constants for simple reactions.

If in the presence of a series of catalysts a process obeys the same kinetic law, the relative reaction rates will be unchanged for different compositions of the reaction mixtures but equal rate constant ratios. It is then convenient to characterise the activity of the catalyst in terms of the rate constant. However, identical rate laws are usually found only for catalysts of similar types and therefore the method of comparing activities in terms of rate constants is not universal.

The identity of the equation implies the equality of the reaction orders with respect to each substance and for equations with several constants it implies in addition the equality of all the constants which cannot be taken outside the function φ. These are, for example, the adsorption coefficients in Balandin's equation [14], which may differ sharply both for the same catalyst of different temperatures and for catalysts of different chemical types [62,63]. Evidently, because of this difference, the result of comparing catalysts in terms of the rate constants of Balandin's equation, for example as in the work of Balandin and Teteni [62], can be actually directly opposed to the result of comparing them in terms of the rate of reaction for a specified reaction mixture composition. Likewise the constant α in Frost's equation can be used as a measure of activity only if the second constants of the equation β are equal, which has been observed [64,65] for catalysts of the same chemical composition subjected to different preliminary treatments.

Sometimes the constant taken outside the function φ can be represented by a fairly complex expression. For example, in first-order reactions investigated in a pulse microreactor, the adsorption equilibrium constant K and a constant k, which is in fact referred to as the reaction rate constant, may be isolated from this overall constant [66]. In this case the product kK is a measure of the activity [67]. The activation energy is also found from the temperature variation of the logarithm of the product kK. [67]

Usually it is assumed that, when different rate laws apply, it is impossible to compare the activities of catalysts in terms of reaction rate constants because these have different dimensions [61]. However, identical dimensions are necessary but not sufficient. Thus, in the equations $v = k$ and $v = kC_A/C_B$, the rate constants have the same dimensions but their ratio is not equal to the ratio of the reaction rates, which depends on the composition of the reaction mixture.

In the case of different power equations, the catalytic activities are sometimes compared [68] in terms of the rate constants, since these are equal to the rates of reaction at unit concentrations (or pressures). Such a comparison refers of course only to a single composition of the reaction mixture and essentially does not differ in any way from the comparison based on the reaction rates. Similar examples can also be found in the studies of homogeneous reactions [69-71]. Apart from unit concentrations, other

compositions of the reaction mixture are sometimes employed[70,71]. Suppose, for example, that the process takes place in the presence of two catalysts according to the equations

$$v_1 = k_1 C_A,\ v_2 = k_2 C_A C_B.$$

Then

$$\frac{v_1}{v_2} = \frac{k_1 C_A}{k_2 C_A C_B} = \frac{k_1}{k_2 C_B},$$

and the activities of the catalyst at a specified concentration of the substance B may be characterised by the rate constants, having multiplied k_2 or divided k_1 by C_B.

The method of comparing activities analysed above, which arose as a result of the work of a number of investigators, is widely employed. The catalysts are compared in terms of the rate of reaction[24,35-38,42-45,56,58,59] and, when the kinetic equations are identical, in terms of the rate constant[65,72-76]. For example, we shall consider the work of Shcheglov et al.[77], who determined the activities of metals in the Fourth Period in the synthesis of ammonia in a flow-circulation reactor. Because of the identity of the kinetic equations for iron catalysts, their activities were compared in terms of the rate constants. Since the equations for other metals were different, the rates of reaction for similar compositions of the gaseous mixture were adopted as a measure of their activity. In those cases where, by virtue of the large difference between the activities it was impossible to obtain comparable data (the catalysts operated in different temperature ranges), the reaction rates were extrapolated by the Arrhenius equation to temperatures at which measurements are impossible.

However, parameters of the kinetic equation and the Arrhenius equation other than the reaction rate or the rate constant are frequently employed as a measure of activity. We shall consider the most widely used of these methods for characterising activity. As will be shown below, many of these are ambiguous and may lead to serious misunderstanding. As in the discussion of the rate constants, the agreement with the results of comparing catalysts in terms of the reaction rates for the same composition of the reaction mixture will be adopted as a criterion of the reliability of the results which they yield.

3. COMPARISON OF CATALYST ACTIVITIES IN TERMS OF THE DEGREE OF CONVERSION

In studies on catalysts, the degree of conversion α, i.e. the amount of substance which has reacted or the yield of products referred to unit amounts of the catalysts, are frequently employed as a measure of activity. The comparison is carried out at a fixed temperature, initial mixture composition, and time in a static reactor or for a fixed duration of contact in a flow reactor§. Under these conditions and in the absence of side reactions, the degree of conversion is proportional to the yield of products. The wide use of the degree of conversion as a measure of catalytic activity can be explained by the ease of its experimental determination. However, one can point to causes which lead to erroneous conclusions and frequently vitiate the results of such investigations.

§ For reactions involving a change in the number of moles, the duration of contact $\tau = \omega/u$ is not usually calculated and therefore the conversions are compared for the same value of w/u_0, i.e. for different values of τ.

A very common error is the assignment of the degree of conversion to a unit amount of the catalyst[78-82]. α is proportional to the amount of catalyst only for zero-order reactions. The proportionality obtains also in the region of low conversions for reactions whose kinetics can be treated approximately as zero-order under these conditions. In all other cases, a change in the amount of catalyst, for example in its surface area, does not entail a proportional change in the degree of conversion. To demonstrate this, we shall consider a plot of α against time (duration of contact) for reactors of different types. Usually this relation is described by a kinetic curve with saturation[83]. The limit to which α tends is independent of the catalyst and is equal to the equilibrium yield for reversible reactions and to total conversion for irreversible reactions¶.

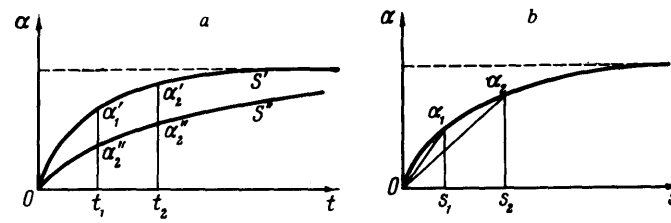

Figure 1. Variation of the degree of conversion with the amount of catalyst: *a*) static reactor; *b*) flow reactor, u_0 = const.

In a static reactor, there is a specific curve relating α to time for each catalyst sample (Fig. 1*a*). For two such curves, the S_1/S_2 ratio is constant and the $(\alpha_1/\alpha_2)_t$ ratio varies with time, since these curves reach the same limit at different rates. Under these conditions for an arbitrarily chosen time, both α/S and the ratio of such quantities for two samples vary along each curve, i.e. $(\alpha_1/S_1)_t \neq (\alpha_2/S_2)_t$. Naturally, the quantity α/S, which depends on the amount of the catalyst, cannot serve as a measure of its activity.

In a flow reactor, it is impossible to determine the variation of α with S or u_0 for a constant contact time, since a change in either of these quantities leads to a change in τ. On the other hand, when S and u_0 are varied simultaneously in such a way that τ remains constant, then α does not vary either. Therefore it is possible to investigate the variation of α with S or u_0 only keeping u_0 or S constant but not τ. The variation of α with $1/u_0$ for two samples of the same catalyst has the same form as the $\alpha - t$ plot for a static reactor (Fig. 1*a*). If the amount of catalyst is varied for a constant rate of supply (of the reactants), the curve shown in Fig. 1*b* is obtained. It is readily seen that in both cases α increases more slowly than S despite the fact that the contact time also increases. Two different catalysts are usually compared for a constant u_0 and volume of the bed. The degree of conversion obtained in such experiments qualitatively characterises the activities of the catalyst volumes employed but it cannot be adjusted for any other volume or any other surface area.

¶ The limiting non-equilibrium yield sometimes observed may be due to the inhibition of the reaction by its products.

In a gradient-free reactor the degree of conversion is proportional to the observed reaction rate and can be referred to a unit amount of the catalyst. However, it would be erroneous to assume that the degrees of conversion obtained for constant rates of supply and compositions of the mixture at the inlet to the reactor may serve as a reliable characteristic of the activity. An increase in the amount of catalyst under these conditions leads to an increase of the observed reaction rate and degree of conversion, i.e. to a change in the composition of the reaction mixture. This in turn entails a decrease of the reaction rate and causes a breakdown of the proportionality between the observed rate and the degree of conversion, on the one hand, and the amount of catalyst, on the other. Therefore comparison of catalysts in terms of the values of α/S is equivalent to the comparison of the reaction rates for different compositions of the reaction mixture.

One can point to examples of unjustified conclusions arrived at by referring α to a unit amount of the catalyst. Tetenyi et al.[84] used a flow reactor to study the activity in three reactions of nickel obtained by different procedures. The conclusion that it had different specific activities was based on a comparison of the amount of unreacted starting material referred to unit catalyst surface. The specific surface of the catalysts varied from 0.5 to 39.3 $m^2 g^{-1}$, i.e. by a factor of 80. Since zero order kinetics were not observed for the reactions investigated, the change in the amount of reactant for identical catalyst samples should be less than the change in surface area, if a constant specific activity is postulated. Indeed the maximum difference between the amounts of starting materials which have reacted is a factor of 12. After referring the conversion to unit surface, catalysts with larger surface areas proved to be "less active". This result provides no information about the constancy or variability of the specific activity of nickel obtained in different ways.

Specific surfaces and activities of $Ni-Al_2O_3$ catalysts according to Swift et al.[85]

Catalyst	Ni, %	$S_{sp\ Ni}$, m^2 g cat.	Activity, % conversion	
			per g of cat.	per m^2 of Ni
$Ni-\eta-Al_2O_3$	6.48	0.58	16.0	27.6
$Ni-\gamma-Al_2O_3$	6.00	1.24	25.0	20.2

Similar objections can be made to a comparison of the activities of two catalysts with the same contents of nickel deposited on η- and γ-Al_2O_3 in the dehydrogenation of cyclohexane[85]. The activity is characterised by the degree of conversion of cyclohexane per gram of catalyst at a constant flow rate through the reactor. The Table shows that the surface area of the active phase in the $Ni-\gamma-Al_2O_3$ catalyst was twice as great, while the degree of conversion of cyclohexane in its presence was higher by a factor of 1.5. After referring α to unit surface of nickel, this catalyst proved to be "less active". To account for the different effects of carriers, the authors investigated their structures and put forward a number of hypotheses. However, the method of comparison which they chose does not allow a decision as to whether there really is a difference between the specific activities of the catalysts investigated.

Unfortunately similar misunderstandings are still encountered fairly frequently on studies of heterogeneous catalysis[86-89].

The lack of proportionality between the degree of conversion and the amount of catalyst is a serious obstacle to the employment of α as a measure of catalytic activity. Naturally, one can point to certain specific problems concerning one particular catalyst, where it is sufficient to know the degree of conversion without referring it to unit catalyst surface. For example, these include tests for the reproducibility of the activity and for the absence of diffusion-dependent inhibition[89], the choice of regeneration conditions[90], the study of the effect of poisons[91] or extraneous substances[92,93], etc. A qualitative comparison of the change in product yield during the experiment and a physical property of the catalyst[94,95] may be accepted, provided that the specific surface remains unaltered in the experiment. However, none of these cases have a direct bearing on the problem of comparing the activities of different catalysts.

As a result of the absence of a proportionality between the degree of conversion and the amount of catalyst, the experimentally determined value of α characterises only the activity of the amount of catalyst employed in the experiment. In a static reactor, it is possible to compare the degrees of conversion obtained during the same period in the presence of different catalysts provided that samples are employed for which the quantitative measure of activity is the same. In a flow reactor samples are also sometimes chosen for which the surface area[96,97], the number of elementary zeolite cells[98], etc. are the same; the comparison is performed at a constant rate of supply. However, owing to differences between the volumes of the catalysts, the comparison in this case involves different contact times.

We shall now point to another cause of the unreliability of characterising catalytic activity with the aid of α determined using an integral reactor. We shall suppose that the amount of catalyst need not be taken into account, since the degrees of conversion during equal periods have been determined for samples with the same quantitative measures of activity, for example the surface area of the active phase. Under this condition, it is also possible to obtain erroneous results, since the ratio of the degrees of conversion is not equal to the ratio of the reaction rates for the same composition of the reaction mixture.

Suppose that in Fig. 2*a* curves I and II refer to two different catalysts taken in identical amounts and catalysing a single process at the same rate. The ratio α_1/α_2, i.e. the ratio of the tangents of the angles ψ_1 and ψ_2, differs appreciably in magnitude from the ratio of the tangents of the angles ψ_3 and ψ_4 defining the slopes of the curves for the mixture composition corresponding to α_1:

$$\left(\frac{\alpha_2}{\alpha_1}\right)_t = \frac{\tan\psi_2}{\tan\psi_1} < \frac{\tan\psi_4}{\tan\psi_3} = \left(\frac{v_2}{v_1}\right)_{\alpha_1},$$

because $\psi_4 > \psi_2$ and $\psi_3 < \psi_1$. Thus the degree of conversion cannot serve as a quantitative characteristic of activity. On the other hand, if the kinetic equations for two catalysts are different, comparison in terms of α can also yield a qualitatively incorrect result. In Fig. 2*b*, α for the upper curve is larger, while the initial rate is also higher but subsequently becomes lower than for the lower curve. If the $\alpha - t$ kinetic curves for two catalysts intersect, the same pattern as in Fig. 2*b* is repeated up to the point of intersection. At the point of intersection the degree of conversion is the same but the rates of reaction are different. In a comparison of the catalysts in terms

of α, the form of the kinetic equation is usually unknown. Therefore there is always a risk that an incorrect result will be obtained, since the equations may be different not only for catalysts of similar composition but even for the same catalyst when the composition of the reaction mixture is changed, as was observed, for example, by Kiperman and coworkers[99,100].

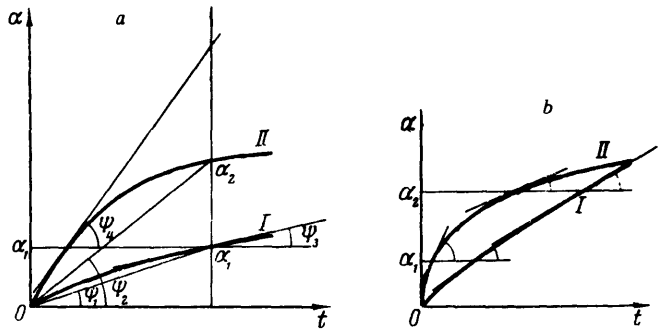

Figure 2. Comparison of the activities of two catalysts in terms of the degree of conversion and reaction rate: *a*) $\alpha_2/\alpha_1 < (v_2/v_1)_{\alpha_1}$; *b*) $v_2 > v_1$ for $\alpha = \alpha_1$ and $v_2 < v_1$ for $\alpha = \alpha_2$.

Thus the method of comparing catalyst activities in terms of degrees of conversion or product yields must be treated with considerable caution. The errors associated with the application of this method are still being encountered in studies on heterogeneous catalysis, although the risk of such errors has been pointed out repeatedly[75,101,102]. Dixon and Webb have reported[103] that, in contrast to heterogeneous catalysis, in the field of enzymatic catalysis comparison of the changes in concentration over a specified period has been completely abandoned in recent years and the method of initial rates is mainly employed.

4. COMPARISON OF THE ACTIVITIES OF CATALYSTS IN TERMS OF THE TIME REQUIRED FOR THE ATTAINMENT OF A GIVEN DEGREE OF CONVERSION

The possibility of a quantitative comparison of catalytic activities in integral reactors without determining the type of kinetic equation, which is provided by the time required for the attainment of a specified degree of conversion as a measure of activity[102], is extremely attractive. It is possible to show[104] that, for $2\alpha - t$ curves described by the same equation, the rate constant ratio is equal to the reciprocal of the ratio of the times required for the attainment of a specified degree of conversion of the starting material when its initial concentrations are the same:

$$\frac{k'}{k''} = \frac{t''_\alpha}{t'_\alpha}. \qquad (7)$$

Therefore the quantity $1/t_\alpha$ is referred to a unit amount of the catalysts[22,105] and is used as a quantitative characteristic of activity. It is evident from Eqn. (7) that the ratio of the quantities t_α for two catalysts is independent of the degree of conversion chosen arbitrarily for comparison in the range of mixture compositions where a single kinetic equation holds (Fig. 3*a*).

For a flow reactor, the contact time w/u_0 [106,107] or the proportional quantities $1/u_0$, G/u_0, [102] Su_0, or G^*/u_0 [108], where G and G^* are the weights of the catalyst and the active phase respectively, etc., are employed instead of time.† Depending on the factor used, different activities are obtained. For the same degree of conversion, the values of $1/u_0$ are proportional to the rate constants corresponding to the total amount of catalyst taken for the reaction, the values of S/u_0 are proportional to the rate constants referred to unit catalyst surface, etc.

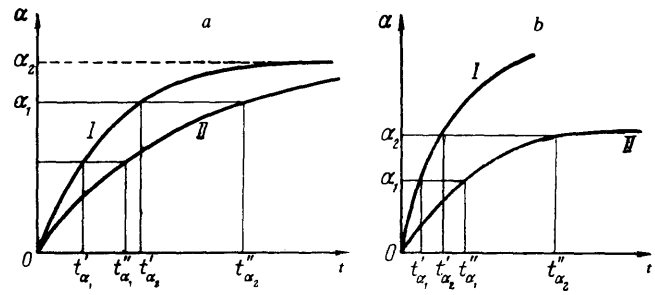

Figure 3. Time required for the attainment of a specified degree of conversion: *a*) $t'_{\alpha_1}/t''_{\alpha_1} = t'_{\alpha_2}/t''_{\alpha_2} = \text{const.}$; *b*) $t'_{\alpha_1}/t''_{\alpha_1} \neq t'_{\alpha_2}/t''_{\alpha_2}$.

Comparison of catalysts in terms of the time required to attain the same degree of conversion is restricted by the same condition as the comparison in terms of rate constants—it is permissible only when the kinetic equations are identical. We may recall that, for an equation with several constants, identity implies the equality of all the constants other than the rate constant. However, if the equation is known, the rate constant is also known and there is no need to replace it by t_α. It is possible to verify the identity of the kinetic equations by a graphical method without determining their form. For this purpose, it is sufficient to superimpose the kinetic curves (Fig. 3*a*) by altering the scale along the abscissa. The constancy of the ratios of t_α for different α can also serve to confirm the identity of the equations. Without such a test, there is always a risk that the equations are different and the method of comparing the activities is inapplicable.

An impression might be created that, regardless of the type of kinetic equation, a higher activity is always associated with a shorter time to attain a specified percentage conversion. That this view is erroneous can be demonstrated with the aid of Fig. 2*b* already examined: t_α for the upper curve is smaller, while the rate of reaction (the slope of the curve) is initially higher and then lower than for the lower curve. If the $\alpha - t$ curves intersect, then at the point of intersection the rates are different while t_α is the same. Thus for different kinetic

† w/u_0 is more correctly called the reciprocal of the space velocity.

equations, comparison of catalysts in terms of the values of $1/t_\alpha$ may be incorrect.

For a reversible reaction investigated at the same temperature in the presence of different catalysts, the same degree of conversion implies also the same degree of deviation from equilibrium and therefore the effect of the reverse reaction on the observed rate of the process will also be the same. The derivation of Eqn. (7), obtained for an irreversible reaction[104], can be extended to this case. For this purpose, it is convenient to employ the criterion of the effect of the reverse reaction γ proposed by Kiperman and Gadzhi-Kasumov[109]. The observed rate of the reverse reaction is

$$v = \vec{k}\vec{\varphi}(C_i)\gamma,$$

where $\vec{k}$ and $\vec{\varphi}(C_i)$ are respectively the rate constant and a function of the concentrations of the reaction mixture components for the forward reaction; γ depends on the degree of departure from equilibrium y. The latter is determined as a fraction of the yield of reaction products relative to the equilibrium value. For the same degree of conversion and an unchanged equilibrium yield, the values of y and γ will also be the same, i.e. Eqn. (7) will hold for a reversible reaction occurring in the presence of two catalysts according to an identical kinetic law.

If the $\alpha - t$ curves have been obtained for the same catalyst at different temperatures, the temperature variation of $1/t_\alpha$ is used to determine the apparent activation energy[41,110,111]. This is valid either when the equilibrium yield in the temperature range investigated is almost constant or for large departures from equilibrium. In the same cases, when the equilibrium yield varies with temperature, an identical degree of conversion is associated with different degrees of deviation from equilibrium and consequently with different values of γ. Then the ratio t'_α/t''_α at two temperatures depends on the value of α (Fig. 3*b*) and cannot be used to calculate the activation energy. The constancy of the activation energy for different α can indicate both[111] the absence of an effect by the reverse reaction and the identity of the kinetic equation in the given temperature range.

5. COMPARISON OF THE ACTIVITIES OF CATALYSTS IN TERMS OF THE TEMPERATURE AT WHICH THE DEGREE OF CONVERSION OR THE REACTION RATE HAS A SPECIFIED VALUE

We shall consider in turn the different variants of the methods for comparing catalysts in terms of the reciprocals of the temperatures at which a particular degree of conversion or reaction rate is attained. The temperature of the onset of reaction[110] is the most indeterminate characteristic of the activity. The experimentally observed onset of reaction depends on the sensitivity of the analytical method and, since it is a quantity lying at the limit of sensitivity, its determination is inaccurate. The possible errors are compounded by the fact that in the region of low conversions a small change in α usually corresponds to a considerable change in temperature. Comparison of the temperatures corresponding to complete conversion is open to similar objections[112].

Therefore it is best to compare the temperatures T_α at which the same degree of conversion is attained in a specified time (the contact time) [113-120] for constant initial concentrations. However, this method has a number of disadvantages associated with the indeterminacy of the degree of conversion as a measure of activity. T_α depends on the amount of catalyst and it is impossible to take into account this relation. Moreover, for integral reactors T_α is not always the temperature at which the catalysts have the same activity because, owing to different forms of the kinetic equation, the same value of α for a constant τ may correspond to different reaction rates.

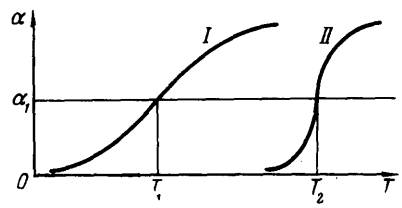

Figure 4. Temperature variation of the degree of conversion.

The variation of α with T for a constant τ is represented by S-shaped curves (Fig. 4, curve *I*)[113,117-120], which are displaced when the rate of supply of the starting material or the amount of catalyst is altered[121]. Takeuchi et al.[120] observed such a sharp increase of α at a specified temperature (curve II) that this temperature was no longer dependent on the amount of catalyst. Therefore they regarded it as a specific characteristic of the catalyst, although the phenomenon might have been associated with the non-isothermal experimental conditions.

In work with reactors allowing the determination of the rate of reaction in a single experiment, the activity is characterised by the temperature T_v, at which the rate of the reaction has a specified value[30,122-125]. Naturally, the comparison must be made for a constant reaction mixture composition. An attempt to employ this method was made by Rubanik et al.[123] in a stirred flow reactor. Deciding against extrapolation of the reaction rate, they adopted as a measure of activity the "temperature at which the same reaction rate, referred to unit catalyst surface, is attained" for constant concentrations of the reactants in the system. However, in fact this characteristic of the activity was not obtained. The surface areas of the catalysts differed at most by a factor of 15. The experiments were performed at a constant volume of the catalyst bed, flow rate, and composition of the gas mixture at the inlet to the reactor. Under these conditions, an identical observed reaction rate v' would imply a constant concentration of all the substances in the system. However, the temperatures were not compared for the same value of v' but for the same value of v'/S, which corresponded to different values of v' and consequently to different compositions of the reaction mixture.

It is possible to avoid the need to allow for surface areas, using catalyst samples for which these areas are the same. It is also possible to achieve the same mixture composition in the reactor for identical values of v'/S by altering the flow rate or the composition of the mixture supplied. The above difficulty of allowing for the amount of catalyst is obviated when the rate of reaction is determined in a differential flow reactor. A constant mixture composition at the inlet and a sufficiently low degree of

of conversion at all temperatures ensure an approximately identical composition of the reaction mixture. This permits a comparison of the temperatures at which the values of $v = v'/S$ are identical.

However, even in the most rigorous variant the reciprocal of the temperature cannot serve as a quantitative criterion of activity in place of the reaction rate, since these quantities are not proportional. In order to justify the use of T_v as a qualitative characteristic of activity, we shall consider the temperature variation of the reaction rate. If for a particular process the same single-term kinetic equation of a power function type holds over a range of temperatures and the Arrhenius law is valid, then

$$v = k\varphi(C_i) = k_0 e^{-E/RT}\varphi(C_i). \quad (8)$$

In this case the temperature variation of the rate constant for a positive activation energy is represented by a rising S-shaped curve. Evidently for a constant composition of the reaction mixture, the $v-T$ plot is also S-shaped. Its specific form is determined by the relative values of k_0, E, and the function φ for specified concentrations. In practice such curves can be readily obtained in a differential flow reactor.

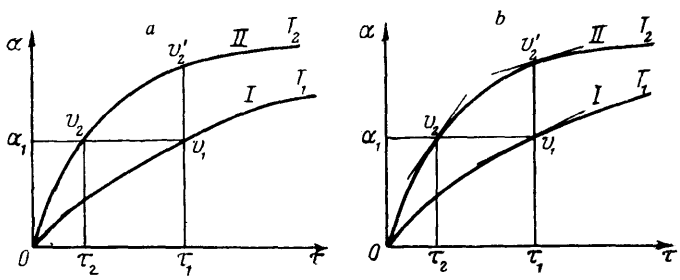

Figure 5. Temperature variation of the reaction rate: *a*) stirred flow reactor; *b*) flow reactor.

In a gradient-free reactor, for a constant contact time and mixture composition at the inlet, the rate of reaction calculated by Eqn. (6) can also only increase with temperature. Suppose that, when the temperature is raised from T_1 to T_2 and α = const., i.e. $\varphi(C_i)$ = const., the rate of reaction increases from v_1 to v_2 (Fig. 5*a*) and the entire curve II lies above curve I, since by our hypothesis they are described by a single equation and cannot intersect. We then increase t_2 to $t_2' = t_1$. The reaction rate v_2' will be higher than v_1, since $\alpha_2' > \alpha_1$.

In contrast to gradient-free reactors, in integral reactors for constant initial concentrations and times (durations of contact) the reaction rate can both increase with temperature and pass through a maximum. Fig. 5*b* shows that $\alpha_2' > \alpha_1$ but $v_2' < v_1$.

Hitherto we have assumed that a single-term power equation holds over a range of temperatures and the activation energy is positive. However, the kinetic equation can contain, apart from the rate constant for the forward reaction, also other constants which depend on temperature (the adsorption coefficients and the rate constants for elementary stages or the reverse reaction). Then both the degree of conversion and the rate of reaction in any reactor are bound to increase with temperature.

Reactions are known with a maximum rate (hydrogenation of olefins[126] and benzene[127]) and degree of conversion (synthesis of ammonia[128]) with respect to temperature. Therefore, for a comparison of catalysts both in terms of T_v and T_α, it is necessary to investigate the variation of v or α with T over a wide temperature range.

The $v-T$ curves for different catalysts may intersect. It has been frequently pointed out[129-131] that temperature is unsuitable as a criterion of activity for different activation energies, since catalysts may be classified as identical or different depending on the rate of reaction chosen arbitrarily for the comparison. There is a risk of arriving at an incorrect result when each catalyst is characterised by a single value of T_v. But if one considers two intersecting curves, the dependence of the result of the comparison on an arbitrarily chosen value of v cannot serve as evidence against the use of T_v as a criterion of activity. The temperature at which the reaction rates are compared is after all chosen just as arbitrarily. At the same time the comparison in terms of T_v yields the same activity series as the comparison in terms of reaction rates at the same temperature, provided that both temperatures and both reaction rates lie on one side of the point of intersection (Fig. 6). Indeed $v_1 > v_2$ and $T_1 < T_2$ but $v_1^* < v_2^*$ and $T_1^* > T_2^*$. When several curves intersect, a more complex pattern may be obtained. Therefore T_v should not be used for the comparison of catalysts with similar activities, particularly since T_v is a less sensitive characteristic than v because of the exponential relation between v and T.

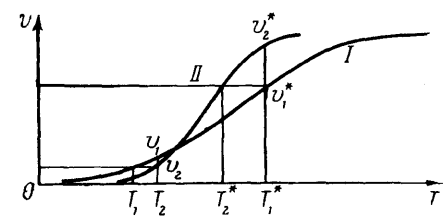

Figure 6. Comparison of the activities of two catalysts in terms of T_v and v.

Thus comparison of catalysts in terms of T_v may yield the correct series of their activities but not their relative values. At the same time the reliability of the results of the comparison in terms of T_α is extremely doubtful, particularly if the differences between the activities are not very great[116] or are absent[132], the $\alpha-T$ curves are not quoted, and there are no data concerning the identity of the kinetic equations.

The use of T_v as a measure of activity is quite justified when a direct comparison of the rates of reaction is impossible because of the different temperature ranges in which the catalysts were used[30]. De Mourgues[30] has mentioned that a comparison of the T_v "yields less quantitative information but is more valid, since it is based on actual and not extrapolated results". This view is shared also by other investigators[125,131,133], although essentially temperature as a measure of activity has no advantages over reaction rates. There may be doubts about the actual values of the extrapolated rate ratios but not about the order of activities based on them.

6. COMPARISON OF THE ACTIVITIES OF CATALYSTS IN TERMS OF ACTIVATION ENERGY

In order to correlate the activities of catalysts with their physical properties, it is extremely desirable to have a characteristic of the activity which depends on the least possible number of process parameters. We shall examine the possibility of using as a kinetic correlation parameter the activation energy—a quantity which is not only independent of the amount of catalyst and the concentrations of the reactants and products but is also constant over a range of temperatures. Although the catalyst reduces the activation energy for the reaction, a reduced value of E cannot be regarded as evidence of higher activity. This method of characterising activity is restricted by a number of conditions. In the first place these are the conditions analogous to those restricting the use of rate constants: (1) if the kinetic equation involves several constants varying with temperature, the activation energy found from the logarithms of the rate constant does not fully reflect the temperature variation of the rate of reaction[1] and cannot therefore replace it as a measure of activity; (2) if different equations hold for different catalysts, then, as shown above, the rate constants cannot serve as a measure of activity and therefore the activation energy is also unsuitable for the purpose of comparison.

Comparison of catalysts in terms of activation energies is possible only when the kinetic equations, with a single temperature-dependent constant, are identical. Eqn. (8) shows that, by virtue of the exponential relation between v and E, the activation energy as well as temperature can serve only as a qualitative characteristic of activity and is less sensitive than the reaction rate.

The last limitation of the method of comparing catalysts in terms of activation energies, which has been frequently pointed out[101,131,134,135], is the necessity to take into account the pre-exponential factor k_0.

Its variability for different catalysts leads to an ambiguous relation between k and E. Indeed, for the same E and different k_0, the activities of catalysts expressed by the rate constants will be different at all temperatures. When E and k_0 vary in parallel (the compensation effect), the linear Arrhenius plots should intersect. Then the activation energy, which is constant over the entire range of temperatures, cannot reflect the reversal of the relative activities at the point of intersection (Fig. 7).

The Arrhenius plot always shows whether the straight lines intersect in the temperature range investigated and whether they can intersect beyond it. The rate constants must then of course be referred to a unit amount of the catalyst.

Thus, for a comparison of catalysts with the aid of activation energies, it is necessary to analyse the relative positions of the linear Arrhenius plots, just as for a comparison in terms of T_V it is necessary to examine the curves relating v to T. Bearing in mind all possible cases of a simultaneous variation of E and k_0 for two catalysts discussed in the literature[136,137], we conclude that the activation energy cannot characterise the activity for parallel or intersecting straight lines when the point of intersection lies in the temperature range investigated or to the right of it.

Thus taking into account the limitations discussed above, the activation energy may be used as a qualitative characteristic of activity. But for the calculation of E, it is necessary to determine initially the rate constant or the rate of reaction over a range of temperatures, which makes it possible to characterise the activity incomparably more accurately without resorting to the activation energy.

The activation energy is employed as a measure of activity mainly in studies dealing with the elucidation of the role of the electronic factor in catalysis. Examples may be found in the reviews of Baker and Jenkins[138] and Schwab[139,140]. When additives are introduced into catalysts (semiconductors or metals deposited on semiconductors), the parallel changes in their activity and electrical properties are compared. The activation energy is determined as a rule from the temperature variation of the initial rate. For equations with a single constant which varies with temperature,

$$\left(\frac{\partial \ln v}{\partial T}\right)_{C_i} = \frac{d \ln k}{d},$$

i.e. when the composition of the gas phase remains unchanged, the apparent activation energy may be determined from the rate of reaction[141,142]. Then, in order to compare the catalysts in terms of the activation energies, account must be taken, instead of k_0, of the variation of v_0—the rate of reaction extrapolated to an infinite temperature. Since for a single-term power equation

$$\lg v = \lg k - \sum n_i \lg C_i,$$

the difference between the $\lg v_0$ is equal to the difference between the $\lg k_0$ when the equations for two catalysts are identical, and the $\lg v - 1/T$ and $\lg k - 1/T$ straight lines intersect at the same temperature.

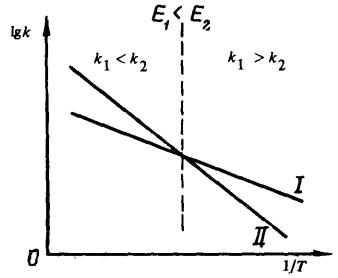

Figure 7. Activation energy as a measure of the activity when linear Arrhenius plots intersect.

When the reaction order changes over a range of temperatures, the activation energies calculated from the rates of reaction[143-145] as well as from the rate constants lose their significance. Therefore it is not surprising that the values of E found for the hydrogenation of benzene on the $Ni-Al_2O_3$ catalyst from the initial rates under the conditions of a variable reaction order and from the rate constants in an equation of the Langmuir–Hinshelwood type are markedly different (16 and 28 kcal mole^{-1}) [143]. There is no reason to regard either of the above quantities as the activation energy for the reaction.

Comparison of catalysts in terms of activation energies is usually not reliable, since it is made without allowance for all the above conditions. The retention of the identical form of the kinetic equation on introduction of an additive into the semiconductor has not been verified[146,147] although the mechanism and processes of semiconductor catalysts may alter under the influence of very small amounts of

impurities. For example, according to the data of Bielanski et al.[68], when 0.1 at. % of iron is added to nickel oxide, the overall order of the CO oxidation reaction changes from first to zero. The change in E is discussed without taking into account the possible change in the pre-exponential factor[146]. Schwab has reported in some papers[148,149] that there is a linear relation between E and k_0 and the temperature corresponding to equal rates for all the catalysts lies above the working range. On the other hand, in other studies this has not been verified[147] or confirmed[148], but E is nevertheless regarded as a characteristic of the activity.

It is clear from the foregoing that it is more desirable to estimate the catalytic activity with the aid of rate constants or reaction rates and the activation energy should be correlated as an energy characteristic of the surface with the activation energy for electrical conduction, electron work function, etc.[74,105]. In correlations of this kind, the variation of k_0 does not play any role, while the remaining limitations remain in force. Teichner[150] concluded that the correlation of the activity with the catalyst properties is best based on the true and not the apparent activation energy, since the change in E on introduction of an additive may be caused by a change in surface coverage and reaction order. The constancy of the reaction order is of course a necessary condition for the comparison of the values of E in the presence of different catalysts but this need not be a zero order and the use of the true activation energy is not necessary.

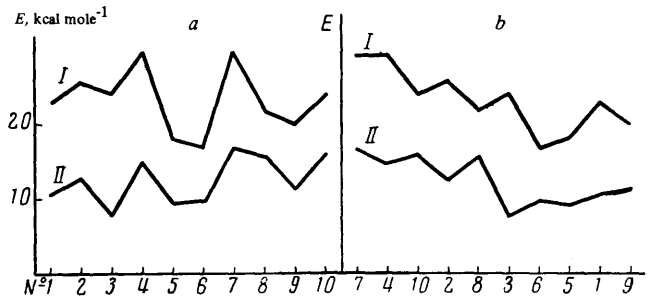

Figure 8. Variation of the activation energy for the dehydrogenation of cyclohexane (curve *1*) and isopropyl alcohol (curve *2*) with the number of the catalyst: a) according to the data of Firth and Holland[152]: *b*) when the order of the catalysts is altered.

The correlation should not be based on the variation with the number of the catalyst arbitrarily assigned by the investigator[84,151,153]. For example, the parallel variation of the activation energies for the dehydrogenation of isopropyl alcohol and cyclohexane in the presence of a series of nickel specimens prepared in different ways[151] can be readily transformed into the opposite variation when the numbers of the catalysts are transposed (Fig. 8).

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Thus we have seen that catalytic activity should be characterised in terms of the reaction rates under rigorously defined conditions. The use for this purpose of other quantities is possible if it is known that the result of their comparison agrees quantitatively or at least qualitatively with the result of a comparison of the rates of reaction at the same temperature and for the same concentrations of all the substances which affect the rate. When this criterion is fulfilled, activity may be characterised, apart from the parameters of the kinetic equation and the Arrhenius equation discussed above, by any other quantity, for example, the rate of evolution of heat when the reaction is performed in a microcalorimeter[152].

Recently attempts have been made to employ correlation analysis for a comparison of the activities of catalysts with their properties. The reaction parameter is the linear relation between free energies yields a general characteristic of the activity of the catalyst for a series of compounds undergoing the same reaction[153,154]. As for the rate constant, its use is restricted by the condition that the kinetic equations must be identical.

We must emphasise that for an accurate expression of catalytic activity, it is sufficient to determine the reaction rates and the knowledge of the mechanism and kinetics of the process does not by itself play a role. Another problem is that in integral reactors the study of kinetics is necessary for the calculation of the reaction rates, while in gradient-free reactors the kinetic equation can be conveniently used to determine the rate of reaction for a specified composition of the reaction mixture. Thus the obligatory need to study the kinetics in order to estimate catalytic activity, which is frequently pointed out[101,137], is valid only for integral reactors.

The aim of a study of catalytic activity can be either practical (the choice of the optimum catalyst and the optimisation of the process) or theoretical (the elucidation of the relation with composition, structure, and physical properties of the catalyst)[3]. In both cases a comparison of the reaction rates is necessary but not sufficient. For the first aim to be achieved, it is in addition important to know the activity of each catalyst under its optimum conditions[155-157,159] and then to decide for which of them the process is more economical.

Attempts are usually made to achieve the second aim by correlating the activity with the properties of the catalyst as a solid. The variation of the reaction rate with concentrations and temperature makes it impossible to characterise the activity also as a property of the solid. "One can speak rigorously only of the catalytic activity characteristic of the entire system, including the catalyst and the reaction mixture"[1]. Therefore the activity should be characterised by a set of reaction rates over a wide range of concentrations and temperatures. Comparison of the activities under one particular set of conditions is insufficient for correlations with the properties of the catalyst as a solid.

In theoretical studies on catalysts, de Mourgues[30] recommends that the simplest reactions be chosen as models. For complex processes, i.e. when several reactions take place simultaneously, the rate of the main reaction or the overall rate of the process may be adopted as a measure of activity.

In conclusion we may note that in the present review the authors endeavoured to describe the present state of the problem and not its history. The review does not pretend to be complete and the choice of specific examples, the aim of which was to make them typical, may inevitably prove to be arbitrary.

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Absorption Spectra of Organic Dyes Containing Two Chromophores

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The Review begins with consideration of the absorption spectra of dyes whose molecules contain non-conjugated (isolated) chromophores. The major portion of the Review, however, is devoted to the spectra of dyes having two conjugated chromophores. According to the view adopted until recently the interaction of conjugated chromophores is apparent in a displacement of the absorption band to longer wavelengths and in an increase in its intensity. The Reviewer and his coworkers have recently established that this view is valid only for the particular case of conjugated chromophores which absorb similar light quanta and lie on the same straight line.

If the light quanta absorbed by the conjugated chromophores are very different, the chromophores do not interact. If the conjugated chromophores are at an angle, their absorption bands do not merge into a single band: on the contrary, they either split or move apart. The intensities of the two new bands are then determined by the angle between the interacting chromophores.

The spectra of bis-dyes which illustrate these principles are examined, and an elementary theory is given for the interaction of conjugated chromophores. A list of 61 references is included.

The concept of colour carriers (chromophores) and of groups of atoms that intensify the colour (auxochromes), which was introduced by Witt into the chemistry of colouring matters almost a century ago, has retained its value until the present time, although we now give a different content to these terms. The name *chromophore* is now applied to a system of conjugated single and double bonds whose presence in sufficient length causes the absorption of visible light even in hydrocarbon molecules. *Auxochromes* are atoms or groups of atoms containing delocalised electron pairs (electron donors—NH_2, NR_2, OH, O^-) and negative [sic] groups of atoms (electron acceptors—NO_2, $CO:NR_2^+$). Auxochromes are located at the ends of the conjugated chain of the dye molecules: donors supply their electrons to the chain of conjugation; acceptors withdraw them.

In the present Review we shall for brevity apply the term *chromophore* to the whole part of the dye molecule which is responsible for its colour, i.e. to the actual chromophore together with the auxochromes (Aux). Thus, when discussing how electronic interaction of two chromophores is revealed in the absorption spectra, we shall have in mind the mutual influence of two systems A and B, both of which absorb visible light, linked together through a series of conjugated or non-conjugated covalent bonds C (Fig. 1) into a single molecule of a bis-dye.

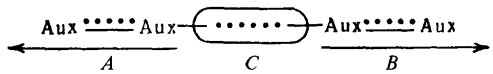


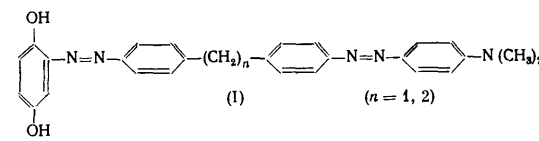
Figure 1.

We shall not be concerned in this Review with the synthesis of the compounds discussed, which can easily be found in the papers cited.

Very many dyes containing two chromophores have been described in the periodical and patent literature, among them the immense group of bisazo-dyes. Unfortunately, only a few such compounds have been examined spectrographically.

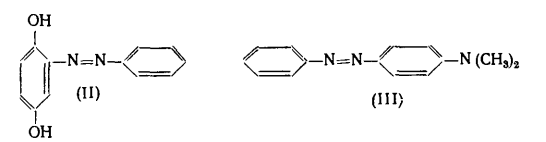
Two chromophores which are separated from each other by saturated groups of atoms ($CH_2.CH_2$, $CH_2.O$, CH_2, etc.) absorb light additively. The absorption spectrum of the solution of such a dye is almost identical with that of a solution of equimolecular proportions of the two corresponding component dyes (parent dyes)[1]. Isolated chromophores absorb light independently of one another: they do not influence each other.

This has been shown by Brode and his coworkers on bisazo-dyes. The absorption curve of the unsymmetrical bisazo-dye (I)



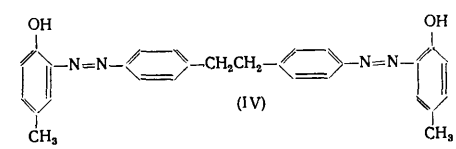
(I) ($n = 1, 2$)

coincides with that of an equimolecular mixture of the two parent monoazo-dyes (II) and (III) [2]



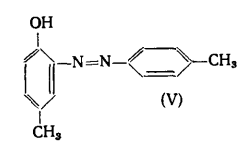
(II) (III)

The spectrum of the symmetrical bisazo-dye (IV)



(IV)

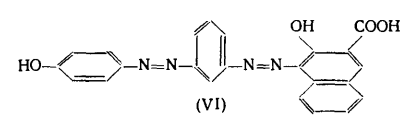
is indistinguishable from that of dye (V)



(V)

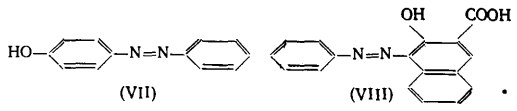
at double the concentration [3].

According to Funkhouser and Brode[4] two chromophoric systems are isolated when linked together through *meta*-positions in a benzene ring: the absorption curve of the bisazo-dye (VI)



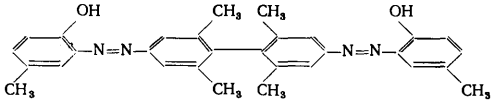
(VI)

is identical with the curve of a mixture of the dyes (VII) and (VIII)



(VII) (VIII)

Isolation of the two azo-chromophores in bisazo-dyes obtained from benzidine derivatives may be due to steric hindrance between the biphenyl rings: the absorption spectrum of the bisazo-dye (IX)

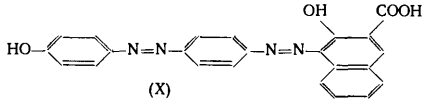


does not differ from that of the bisazo-dye (IV) [5].

All that has been said about the spectra of bisazo-dyes containing isolated chromophores applies also to bis-dyes of other classes—bismerocyanines[6], bisazomethines[7], etc.

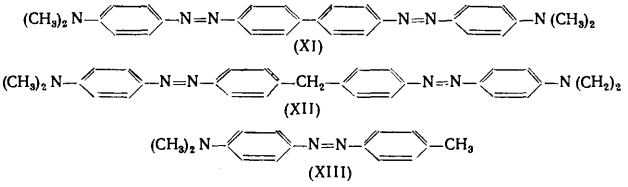
We shall not deal in this Review with the vast number of papers by the eminent Soviet scientist V. A. Izmail'skii, in which he showed that an intense colour can arise also when two auxochromes (donor and acceptor of electrons), present in the same molecule, are isolated from each other by saturated groups of atoms. This type of coloration is observed only in the solid state and in concentrated solutions. It is due not to intramolecular electron transitions but to intermolecular exo-interactions of donor and acceptor groups, and is explained by the formation of complexes with partial transfer of charge. If two chromophores in a dye molecule are not isolated from each other, but are in some measure conjugated, the absorption spectrum usually differs markedly from those of the component dyes. According to ideas current until recently the interaction of conjugated chromophores is shown by a shift in the absorption band to longer wavelengths and in an increase in the intensity of absorption[8].

Brode and his coworkers showed, for example, that the bisazo-dye (X)



(X)

in which the arylazo-groups are interlinked through a *para*-phenylene ring, absorb considerably further towards the red end of the spectrum and more strongly than the isomer (VI), in which the same chromophores are joined in the *meta*-position[4]. Fig. 2 shows the absorption curves† of two symmetrical bisazo-dyes (XI) and (XII) and also of the corresponding component dye (XIII) (at double the concentration). Here, too, a bathochromic shift in the band due to dye (XI) is clearly evident in comparison with the bands of dyes (XII) and (XIII), which show close similarity[3].



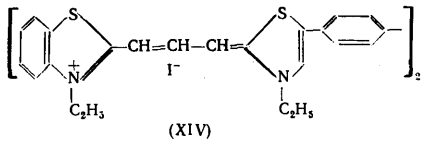
(XI)

(XII)

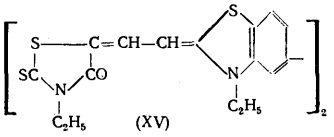
(XIII)

† Here and subsequently absorption curves and maxima are given for alcoholic solutions, where no solvent is specially mentioned.

A similar deepening of colour has been observed in symmetrical biscyanines (XIV) [9] and bismerocyanines (XV) [10]



(XIV)



(XV)

in comparison with the corresponding mono-dyes.

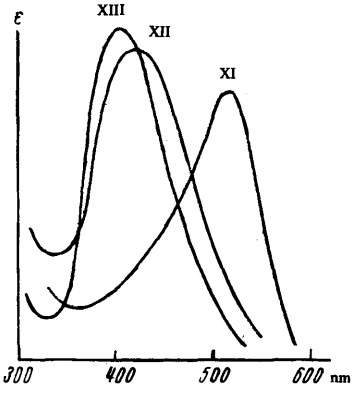
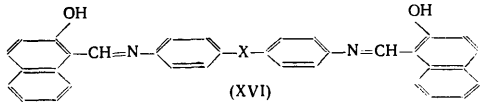


Figure 2.

The effect of the nature of the bridge X on the degree of conjugation between azomethine chromophores has been investigated on bisazomethines of formula (XVI) [11]



(XVI)

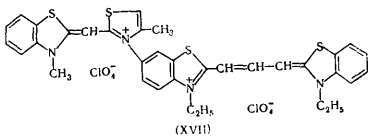
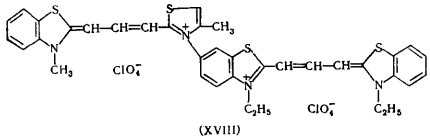
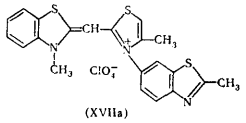
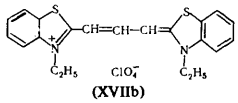
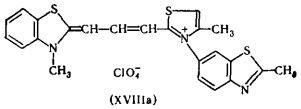
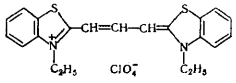
Table 1.

X	Abs. max., nm	$10^{-4}\varepsilon$	X	Abs. max., nm	$10^{-4}\varepsilon$
CH_2	345	2.86	S	358	3.70
O	350	3.60	NH	413	4.83

Such conjugation is apparent in a displacement of the absorption maximum (abs. max.) and an increase in molecular extinction. Table 1 shows that oxygen, sulphur, and nitrogen atoms, with their lone pairs of electrons, do not have an isolating effect like that of the methylene group. However, the effect of conjugation through bridges of this type is relatively small in bisazomethines, as well as in bisazo-dyes[12,13] and in biscyanines[14].

We shall not cite other published examples of the interaction of bound chromophoric systems. The view held until recent years was that two conjugated chromophores in a dye molecule lose their individuality, delocalise into one conjugated system, and absorb light as a single chromophore having a longer conjugated chain. As a result the absorption bands corresponding to each individual chromophore merge to form a single more intense band displaced to lower frequencies[15].

Table 2.

Biscyanines	Abs. max., nm
 (XVII)	422 563
 (XVIII)	581 522
Component cyanines	**Abs. max., nm**
 (XVIIa)	420
 (XVIIb)	558
 (XVIIIa)	562
 (XVIIIb)	558

It has been found recently, however, that this view is valid only for the particular case in which the conjugated chromophores when separated (in the parent dyes) absorb closely similar light quanta, and also when these chromophores lie on the same straight line (Fig. 1). If the quanta absorbed by the two chromophores differ greatly, the chromophores do not interact at all, even when conjugated with each other. If the conjugated chromophores do not lie on a straight line, but are inclined at an angle, their absorption bands do not merge into a single band, but on the contrary split or move apart. The intensities of the two new bands will then depend on the angle between the interacting chromophores. We shall now discuss these previously unknown phenomena.

In 1964 Kiprianov and Mushkalo[16] synthesised six biscyanine dyes in which the nitrogen atom of the thiazole ring of one cyanine was covalently bound to the benzothiazole ring of a second cyanine. Two biscyanines of this type—dyes (XVII) and (XVIII)—are given as examples in Table 2. The absorption spectra of each of the six biscyanines of this series contained two intense bands. It would naturally be assumed that the maxima of these bands would approximate in some measure to those of the corresponding parent dyes, which were also prepared (e.g. XVIIa and XVIIb in Table 2). However, comparison of the absorption maxima of the biscyanines with those of the corresponding parent dyes led to an unexpected result.

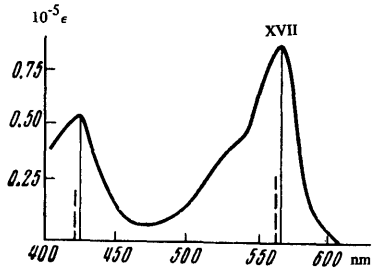


Figure 3.

With biscyanines in which the two chromophoric chains differed in length, e.g. (XVII), the maxima on the absorption curve (Fig. 3) almost coincided with those of the corresponding component dyes (XVIIa) and (XVIIb) (these maxima are indicated by the broken lines in Fig. 3). This implies that the chromophores in such biscyanines do not interact, although they are conjugated.

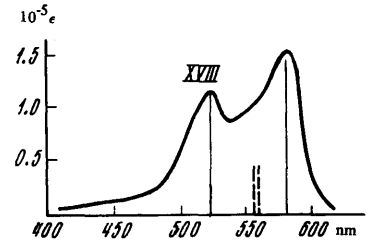


Figure 4.

With biscyanines which contain two chromophores of the same length, e.g. (XVIII), on the other hand, the maxima on the curve (Fig. 4) differed markedly from the absorption maxima of their component dyes (denoted by broken lines). The shorter-wavelength maximum of the biscyanine was shifted to still shorter wavelengths, and the longer-wavelength maximum to still longer wavelengths, than in the component dyes. Thus the chromophores in biscyanines with polymethine chains of the same length interact. The interaction, however, does not lead to coalescence of the absorption bands but to their

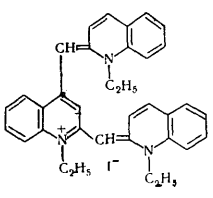
moving apart (or resolution, as has since been shown with biscyanines of symmetrical structure).

Despite the paucity of experimental results these workers[16] permitted themselves the conclusion that the interaction of two conjugated chromophores depends on the light quanta which each chromophore absorbs separately. If the quanta differ greatly, the chromophores do not interact. If the quanta differ little, the chromophores interact in such a way that the frequency absorbed by one chromophore increases, while that absorbed by the other decreases, the absorption bands moving apart. The authors mention the theory of perturbations and its application to electronic spectra[17].

Kiprianov and Dyadyusha[18] examine the physical nature of these phenomena, starting to a first approximation from the principles of classical wave mechanics. Two conjugated chromophores are two coupled oscillators, analogous e.g. to two loosely connected pendulums. If such pendulums differ in length, they have little influence on each other, and each oscillates at its characteristic frequency. But if the pendulums have the same or similar lengths, they interact, which is apparent in a change in their vibration frequency. When isolated from each other, the pendulums oscillated at frequency ν; now that they are coupled, they are able to oscillate only at the two new frequencies $\nu - e$ and $\nu + e$. In one case oscillations of the pendulums are in phase; in the other case they are of opposite phase.

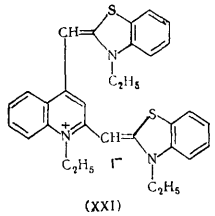
Electrons oscillate in the conjugated chromophores of bis-dyes. If the vibration frequencies of the electrons in the isolated chromophores are the same or similar, the conjugation of such chromophores should result in their vibration and absorption of light at two new frequencies, one higher and the other lower than the original frequency.

Two cases are known of the observation by other workers of analogous phenomena to those observed by Kiprianov and Mushkalo above. In 1953 Shibata[19] prepared the distyryl dye (XIX) and the corresponding two monostyryl dyes (XIXa) and (XIXb) (Table 3). He took no notice of the fact that the bands corresponding to the monostyryl derivatives had moved apart in the spectrum of the distyryl compound. Perhaps this was because such separation was inconsistent with his quantum-mechanical calculations.



(XX)

Abs. max. 615, 480 nm (550, 520 nm)

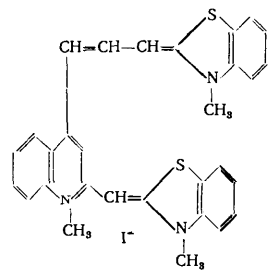


(XXI)

Abs. max 547, 450 nm (509, 480 nm)

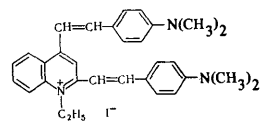
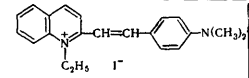
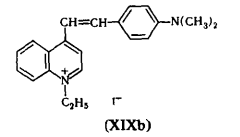
Still earlier Brooker and Smith[20] had noted something similar in the spectra of the two biscyanines (XX) and (XXI). With both dyes the two absorption maxima were farther apart than those of the corresponding monocyanines (indicated in parentheses). The authors tried to explain why the longer-wavelength bands of their dyes had shifted towards the red end of the spectrum, but the displacement of the shorter-wavelength bands in the opposite direction remained incomprehensible to them.

Kiprianov and Mushkalo showed[21] that the parting of the absorption bands in the spectra of Brooker and Smith's biscyanines was due to the same cause as in the spectra of the biscyanines which they themselves had described[16]. While it is true that the two chromophoric chains in (XX) and (XXI) differ in length and that the absorption maxima of the corresponding component dyes do not coincide, it must be borne in mind that conjugation of the chromophores, including the common methine groups, is far stronger here than in Kiprianov and Mushkalo's bis-dyes. In fact it was found that in the spectra of dyes of the same type, but with a still greater difference in length between the chromophoric chains, e.g. in the spectrum of the biscyanine (XXII)



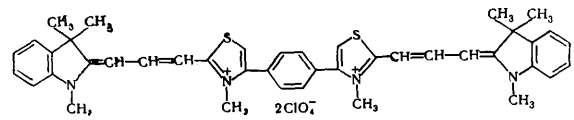
(XXII)

Table 3.

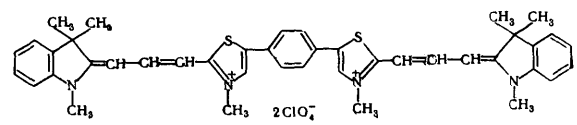
Distryl dye	Abs. max., nm	Monostyryl dye	Abs. max., nm
 (XIX)	500 570	 (XIXa)  (XIXb)	527 546

there is hardly any separation of the absorption maxima relative to those of the component dyes.

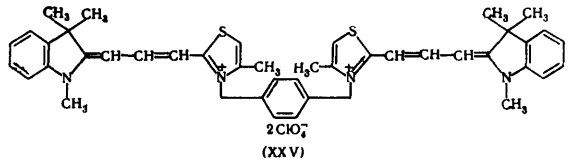
The biscyanines in which the separation of absorption bands due to conjugated chromophores was discovered proved to be a convenient subject for studying the new phenomenon. This applies especially to symmetrical biscyanines, in which the bands due to the two identical component dyes do not move apart but are resolved.



(XXIII)



(XXIV)



(XXV)

have been synthesised[22]. Figs. 5–7 show their absorption curves (full lines) and those of the corresponding parent monocyanines (XXIIIa)–(XXVa) (broken curves). The curves for (XXIII) and (XXIIIa) (Fig. 5) have the same shape and the same position of the maxima, differing only in intensity. The chromophores in the molecule (XXIII) are not formally conjugated, and hardly interact at all. In contrast, curves (XXIV) and (XXIVa) in Fig. 6 are completely different: here the chromophores are conjugated, so that the band of the parent cyanine is split in the spectrum of the biscyanine into two new bands of different intensities. Interaction between the chromophores is observed also in the biscyanine (XXV) (Fig. 7), but it is far weaker, and the two bands have moved apart less.

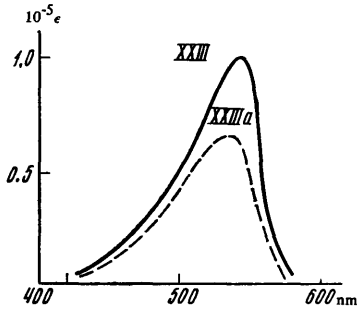
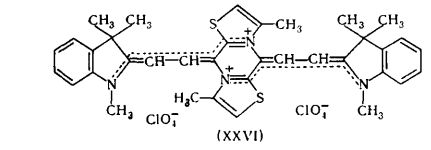
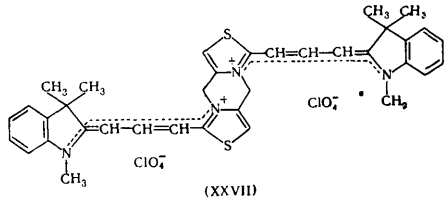


Figure 5.

It has been shown[23] how different are the spectra of biscyanines with conjugated and non-conjugated chromophores by the synthesis of two biscarbocyanines (XXVI) and (XXVII)

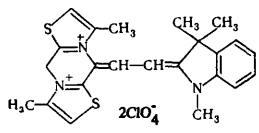


(XXVI)

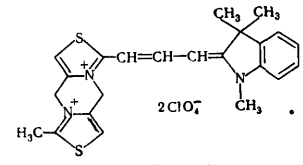


(XXVII)

of generally similar structure together with the corresponding parent cyanines (XXVIa) and (XXVIIa)



(XXVIa)



(XXVIIa)

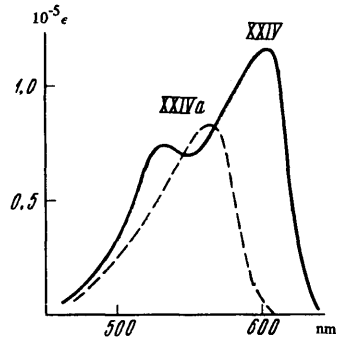


Figure 6.

The chromophoric chains in the bis-dyes are shown as broken lines in the structural formulae. They are conjugated in the first of these biscyanines, but separated by methylene groups in the second biscyanine.

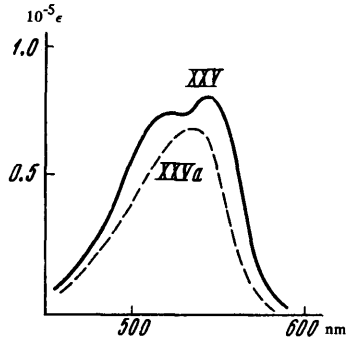


Figure 7.

Fig. 8 shows the absorption curve of the biscyanine (XXVI) and the absorption maximum of the component cyanine (XXVIa) (broken curve). This is a typical picture of strongly interacting chromophores: the absorption bands of the cyanine (XXVIa) (maximum at 552 nm) are split into two mutually remote bands (maxima at 490 and 642 nm).

Fig. 9 shows that the absorption curves of the biscyanine (XXVII) and the component cyanine (XXVIIa) are very similar in shape, with only one band of almost double

the intensity in the biscyanine. Both indicate absence of interaction between the chromophores, but the biscyanine maximum is displaced 19 nm to longer wavelengths. Consequently the methylene group does not completely isolate the chromophores in this case, some mutual influence being preserved.

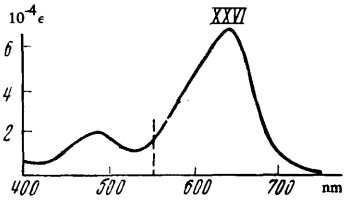


Figure 8.

It must be supposed that the degree of interaction of the chromophores in bis-dyes is defined by the increase in separation or the resolution of their absorption bands. If we denote by Δ_1 the difference between the absorption maxima of the two component dyes and by Δ_2 the difference between the maxima of the two bands of the bis-dye, the degree of interaction of the chromophores in the latter should be measured by $\Delta = \Delta_2 - \Delta_1$. In the case of bis-dyes of symmetrical structure $\Delta_1 = 0$ and $\Delta = \Delta_2$.

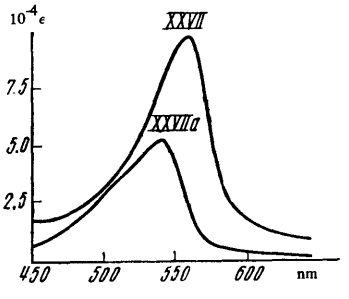
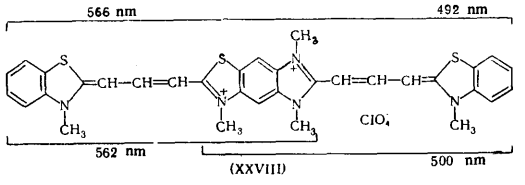


Figure 9.

In order to elucidate the factors determining the degree of interaction of chromophores in biscyanines, a series of nine dyes of the type (XXVIII)

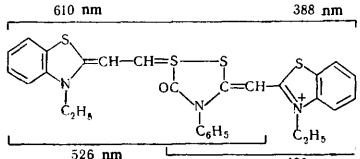


(XXVIII)

and the corresponding parent monocyanines were prepared[24,25]. Above the formula of the bis-dye (XXVIII) are indicated the maxima of its two absorption bands, and below the formula those of the component monocyanines. In the present case the maxima move apart by $\Delta = 12$ nm. Both central and terminal heterocycles were varied in biscyanines of this type, the corresponding Δ values being determined each time.

This work confirmed the correlation already mentioned between the increase Δ in the separation of the absorption maxima of the chromophores in the biscyanines and the difference Δ_1 in the maxima of the component cyanines: the smaller is Δ_1 the larger is Δ. The mutual withdrawal of the bands is largest in symmetrical biscyanines. The interaction of the chromophores is influenced also by the mobility (degree of delocalisation) of the π-electrons in the polymethine chromophore: the more delocalised are these electrons, the more strongly the chromophores interact‡. However, there is yet another important factor influencing the increased separation of absorption bands in dyes having conjugated chromophores. It can be termed "the degree of conjugation of the chromophores", a name which has not yet been fully defined.

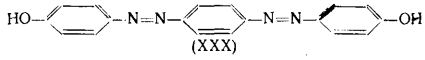
An example of bis-dyes with a high degree of conjugation between the chromophores is provided by the trinuclear rhodacyanines[27]. Spectroscopic investigation[21] of the dye (XXIX)



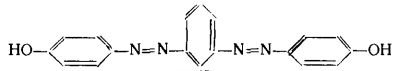
(XXIX)

showed that, despite the very large difference between the maxima of the two component dyes of this rhodacyanine ($\Delta_1 = 87$ nm) and the absence of formal conjugation between the polymethine chains, the mutual withdrawal Δ of the maxima reaches 135 nm. The probable reason for such strong interaction of the chromophores through the rhodanine ring is that this ring is present in both component dyes. Investigation of a series of analogous trinuclear cyanines (bismerocyanines) shows[28] very considerable withdrawal of the absorption bands in all of them, which is also larger the smaller the difference between the maxima of the component dyes.

Hitherto we have been considering the resolution of absorption bands in biscyanine dyes. However, this phenomenon should be common to bis-dyes of all classes. It seemed surprising that it had not been noted in any of the many known bisazo-dyes. It was therefore of especial interest to study, more carefully than had been done previously, at least the simplest members of this immense group of colorants. In 1968 the two bisazo-dyes (XXX) and (XXXI)



(XXX)



(XXXI)

were investigated spectroscopically[29].

Fig. 10 shows the absorption curves of the bisazo-dye (XXX) and of the component dye *p*-hydroxyazobenzene (XXXa). These curves were obtained in alcohol alone (full curves) and with added alkali (broken curves). In both solvents we observe the long known pattern: the

‡ The degree of delocalisation of π-electrons in unsymmetrical cyanines is determined by their deviation[26].

bands of the bis-dye are displaced to longer wavelengths, especially in the alkaline solution§. No splitting of the band is seen in the bisazo-dye (XXX).

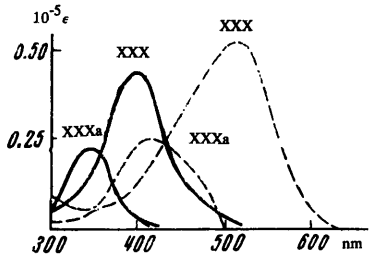


Figure 10.

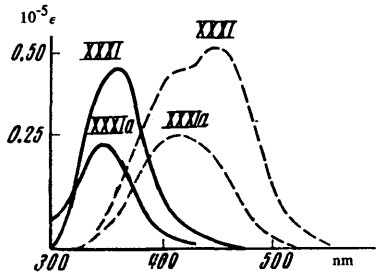


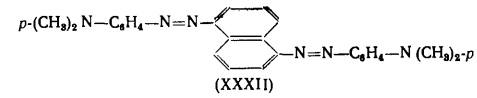
Figure 11.

The absorption curves of the bisazo-dye (XXXI) in neutral and alkaline alcoholic solutions are at first glance unexpected (Fig. 11). Here the two azo-groups are linked through the *meta*-position of a benzene ring, so that formally they are not conjugated. Nevertheless, the absorption band of the bisazo-dye (XXXI) is displaced towards the red end of the spectrum with respect to that of the component dye (XXXa)¶, and in alkaline solution there is even appreciable resolution into two bands. It has also been shown in several other experiments—dyes (XLIII), (XLVII), (LVI), and (LVII)—that the interaction of chromophores linked through the *meta*-positions of a benzene ring is weak but not entirely absent. The situation is probably similar to that observed with rhodacyanine dyes. As we shall see later, the absence of band splitting in the bisazo-dye (XXX) and its presence in (XXXI) are connected with the linear structure of the former molecule and the angular structure of the latter.

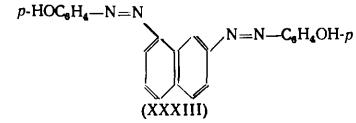
§ Delocalisation of π-electrons is greater in dye anions and cations than in the unionised molecules[26].

¶ Although Brode had stated[4] that azo-chromophores in *meta*-positions do not influence each other.

The interaction of two azo-chromophores has been studied also in the bisazo-dyes from naphthylene-1,5-diamine (XXXII) and from naphthylene-1,7-diamine (XXXIII)[30]



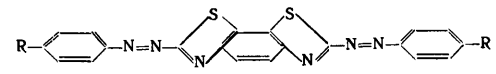
(XXXII)



(XXXIII)

Contrary to earlier results[31], no conjugation has been detected between the azo-chromophores in the spectrum of the bisazo-dye (XXXII). On the other hand, the chromophores are conjugated in (XXXIII), as is seen from the distinct splitting of the absorption band (angular molecular structure).

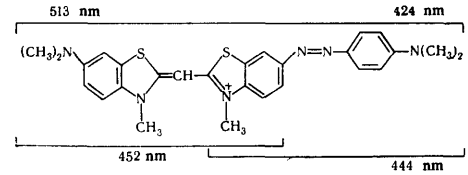
Two bisazo-dyes have been prepared from thiazolobenzothiazolediamine—(XXXIV) and (XXXV)[32]



(XXXIV: R=OH) (XXXV: R=N(CH3)2)

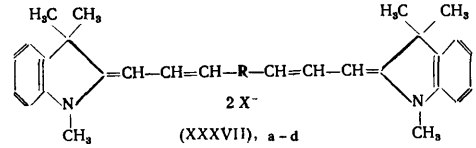
Both these symmetrical bisazo-dyes show, in neutral alcoholic solution and still better in alkaline (XXXIV) or acid (XXXV) solutions, the splitting of the absorption band of their component dyes which is typical of conjugated bis-dyes.

The interaction of a polymethine chromophore with an azo-chromophore has been studied[33] in azo-cyanine dyes. Here, too, maximum interaction was observed in dyes where the two component dyes absorbed similar light quanta, e.g. (XXXVI)



(XXXVI)

Very interesting results on the band intensities of dyes containing two conjugated chromophores were obtained[34,35] from an investigation of the spectra of biscyanines synthesised from isomeric dimethylthiazolobenzothiazoles. Four isomeric bistrimethinecyanines (XXXVII)



(XXXVII), a–d

were obtained, in which the central ring R was one of the fused systems (a)–(d) (Fig. 12), as well as several other symmetrical biscyanines and distyryl derivatives containing the same ring systems (a)–(d). The absorption curves of the biscyanines (XXXVIIa–d) are reproduced in Fig. 13.

The spectrum of the biscyanine (XXXVIIa) was found to contain two bands *a* and *a'* of almost equal intensity; with (XXXVIIb) the intensity of the shorter-wavelength band *b'* fell, whereas the longer-wavelength band *b* increased sharply in intensity; the shorter-wavelength band *c'* of the biscyanine (XXXVIIc) was hardly noticeable;

and finally (XXXVIId) exhibited only a strong longer-wavelength band *d*, while the shorter-wavelength band had almost disappeared†. Comparison of the structural formulae of these biscyanines (XXXVIIa–d), taking into account X-ray data on the thiacyanines [38,39], clearly reveals a correlation between the intensity ratio of the two bands of each biscyanine and the angle between the directions of its polymethine chromophores (from one auxochrome to the other). This angle is smallest (80°) in the isomer (XXXVIIa) (Fig. 14); it is 180°, i.e. a maximum, in (XXXVIId), whose molecule is centrosymmetric.

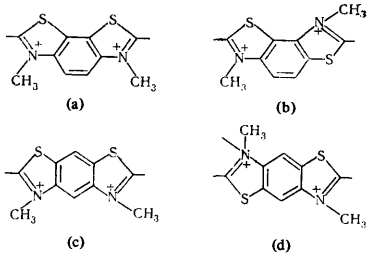


Figure 12.

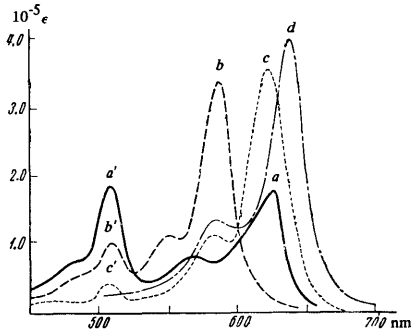
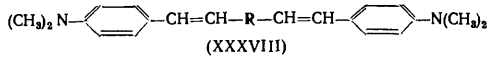


Figure 13.

The intensity ratio of the two bands in the biscyanine (XXXVIIa) remains almost unchanged with increase in the length of its chromophoric chains. In the distyryl dye (XXXVIII)

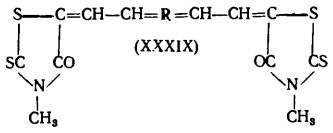


(XXXVIII)

containing the same central ring (R = a), however, the intensity of the longer-wavelength band, in contrast to the biscyanine (XXXVIIa), is almost double that of the shorter-wavelength band (Fig. 15). In fact, the angle between the chromophoric chains is far larger in (XXXVIII) than in (XXXVIIa) (Fig. 16).

† Inflexions on the short-wavelength portion of the absorption curves, in the present case in the range 550–600 nm, are characteristic of most cyanine dyes and are due to vibrational transitions [36]. This origin of such inflexions has recently been proved by the luminescence spectra at low temperatures [37].

Investigation of the spectra of the bismerocyanines (XXXIX)



(XXXIX)

where R represents one of the ring systems (a)–(c) (see above) revealed the same dependence of the intensities of the absorption bands on the angles between the chromophores [40].

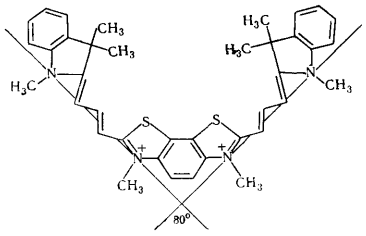


Figure 14.

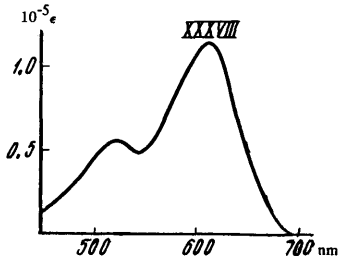
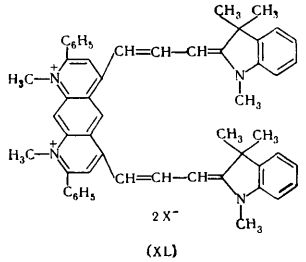


Figure 15.

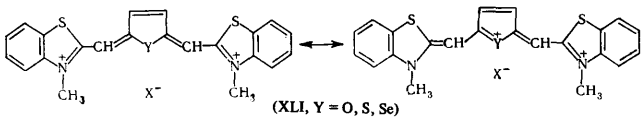
In 1968 it proved possible to synthesise [41] the first biscyanine (XL) in which the directions of the chromophoric chains formed an acute angle



(XL)

In conformity with expectation the shorter-wavelength band of this dye was considerably more intense than the longer-wavelength band (Fig. 17). Since then simpler bis-dyes have been obtained with acute angles between the chromophores—see (XLII) and (XLVI).

Unusual bis-dyes of general formula (XLI)



(XLI, Y = O, S, Se)

have recently been described[42]. Fig. 18 shows that two bands—a more intense longer-wavelength band with a fine structure and a weaker shorter-wavelength band—are present in the absorption spectra of all three compounds.

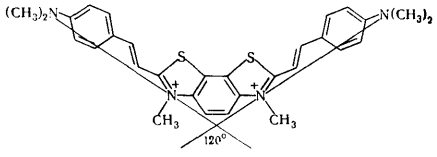


Figure 16.

This corresponds to obtuse angles between the chromophores. The intensity ratio of the two bands indicates that the selenophen derivative has the largest angle and the furan derivative the smallest: this was to be expected. Similar observations have been made[43] on biscyanines obtained from dimethyloxazolobenzoxazole and dimethylthiazolobenzothiazole.

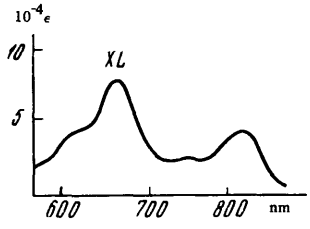


Figure 17.

The experimental results discussed in this Review leave no doubt that the intensity ratio of the two absorption bands which appear on electronic interaction between two combined chromophores is determined by the angle between the chromophores in space‡.

The elementary theory of the interaction of chromophores (Kiprianov and Dyadyusha[18,44]) is consistent with this generalisation. The oscillations of a positive or a negative charge excited in the chromophores by the alternating electric field of a light wave are equivalent to vibrations of a dipole. Because of the repulsion of like charges, the excitation of oscillations in which the like charges in chromophores joined at the ends come together (*a* and *d* in Fig. 19) requires more energy than with the opposite phase relationship (*b* and *c*). The former corresponds to high-frequency or short-wavelength absorption bands, the latter to low-frequency or long-wavelength bands.

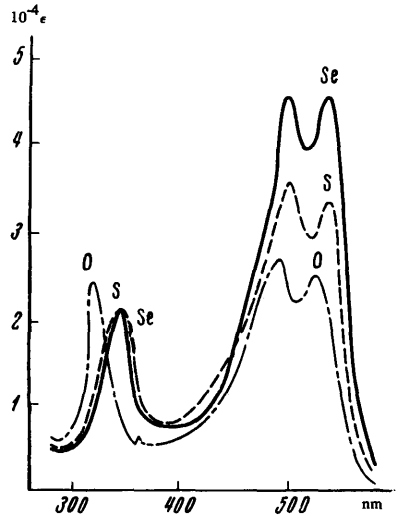


Figure 18.

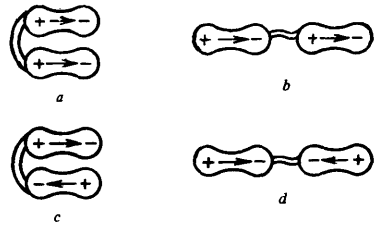


Figure 19.

If the angle between the chromophores is either 0 or 180°, the oscillations depicted as *a* and *b* (Fig. 19) are equivalent to vibrations of a dipole having double the charge. They interact strongly with the field of the light wave. With oscillations of types *c* and *d*, on the other hand, the aggregate dipole remains unchanged, and these vibrations cannot be actively involved in the absorption of light. With the chromophores arranged parallel (angle 0°), therefore, only the short-wavelength band can be intense. If, however, one chromophore constitutes a prolongation of the other (angle 180°), only the long-wavelength band can be intense. With intermediate angles between the chromophores (Fig. 20) both absorption bands should be observed, with the short-wavelength band more intense at acute angles, and the long-wavelength band at obtuse angles.

It is desirable that models for study of a new phenomenon should be as simple as possible. In the case of

‡ At least in bis-dyes of symmetrical structure. The intensities of the component dyes must also be taken into account in the case of unsymmetrical bis-dyes.

dyes having two linked chromophores this condition was met by bishemicyanines. A considerable number of dyes of this group have been reported in the patent literature[45], but their absorption spectra have not been investigated.

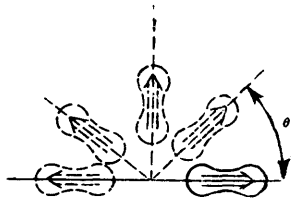
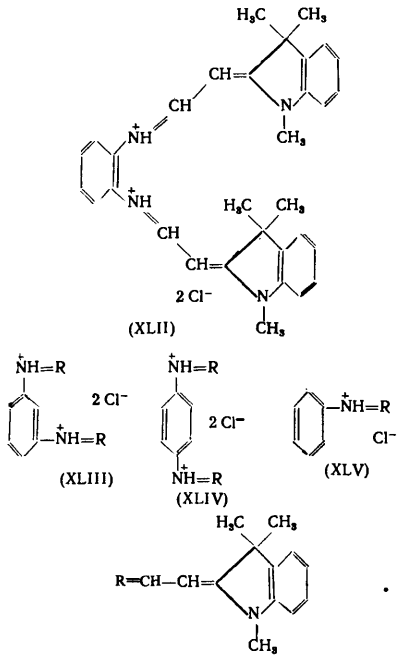
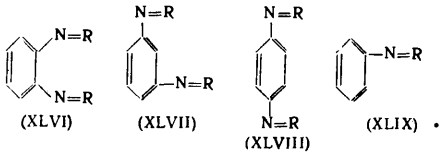


Figure 20.

Kiprianov and Buryak[46] determined the absorption curves of three simple isomeric bishemicyanines (XLII)–(XLIV) and also that of the component hemicyanine (XLV). We give the structure of the first of these dyes in full, and the other structures in abridged form:



These dyes are converted by alkali into the corresponding bases (XLVI)–(XLIX)



The absorption curves of these bases show (Fig. 21) that the chromophores interact in every case. In the spectrum of the *ortho*-derivative (XLVI) the band of the component base (XLIX) is split into two new bands, of which the shorter-wavelength band is by far the more intense. This intensity relationship was to be expected, since the two chromophores should form an acute angle in this *o*-phenylenediamine derivative.

No splitting of the band due to the component hemicyanine is observed in the spectrum of the base (XLVII) (a derivative of *m*-phenylenediamine). However, the chromophores do interact, as is evident from the shift in the band to longer wavelengths.

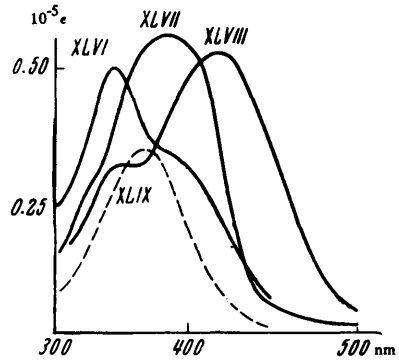


Figure 21.

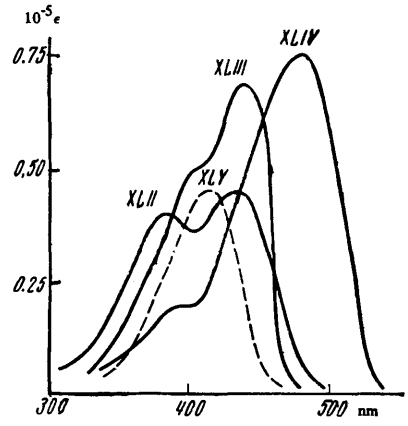


Figure 22.

In the base (XLVIII) the chromophores are conjugated, but they are arranged in diametrically opposed directions. Here an intense long-wavelength band would be expected with disappearance of the short-wavelength band. Nevertheless, although the former is strong, we see also a weak but distinct short-wavelength band. It is probable that not all the equilibrium conformations of this molecule have a centrosymmetric structure§.

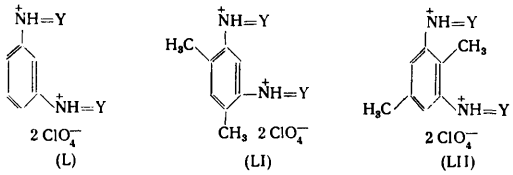
Fig. 22 shows the absorption spectra of the bishemicyanines themselves (XLII)–(XLIV) and of the hemicyanine (XLV). As usual, the absorption bands of the salts

§ Like the dimethyl ether of quinol, in which the dipole moment differs from zero.

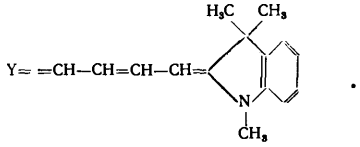
are more intense than those of the bases, and are displaced towards the red end of the spectrum. The absorption curves underwent interesting changes on passing from the bases to the salts. The longer-wavelength band—not the shorter-wavelength band—is more intense in the spectrum of the *ortho*-derivative (XLII) in contrast to the spectrum of the base (XLVI). The appearance of like cationic charges on the nitrogen atoms pushed the latter apart. The absorption curve of the *meta*-derivative (XLIII) exhibits not only a general shift in the band to longer wavelengths but also a distinct splitting with the formation of a shorter-wavelength maximum, in spite of the absence of formal conjugation. The absorption curve of the *para*-derivative (XLIV) resembles that of the corresponding base (XLVIII).

The spectra of bishemicyanines revealed steric effects on the introduction of methyl groups *ortho* to the chromophoric chains. These effects are readily evident in the methyl and dimethyl derivatives of the bishemicyanines just described[47], but they become especially strong as the polymethine chromophores become longer. Let us give a few examples[48].

m-Phenylenediamine and its dimethyl derivatives have been used to prepare the bishemicyanines (L)–(LII)



where



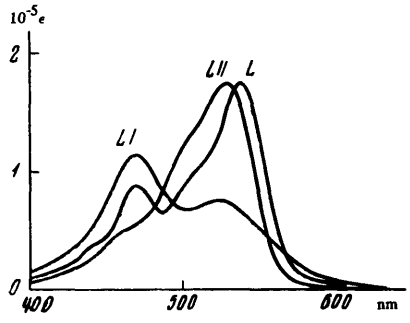
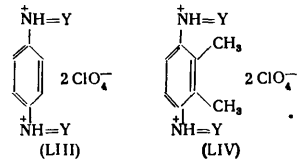


Figure 23.

From Fig. 23 it can be seen how the volume of the methyl groups affects the angle between the chromophores. The intensities of the absorption bands indicate that, as was to be expected, this angle is obtuse in the bishemicyanine (L). The introduction of two methyl groups into positions 4 and 6 of the benzene ring (bishemicyanine LI) forces the chromophoric chains together and makes the angle between them acute. But if a methyl group is placed between the chromophores (dye LII), the angle between them increases almost to 180°.

Similar changes in angle between the chromophores under the influence of adjacent methyl groups are observed also in the bishemicyanine from *p*-phenylenediamine (LIII) and its dimethyl analogue (LIV)



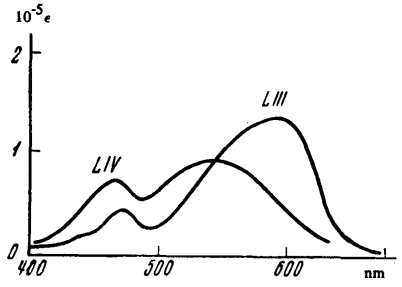
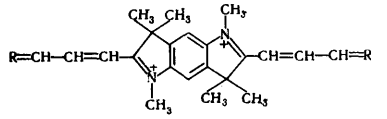
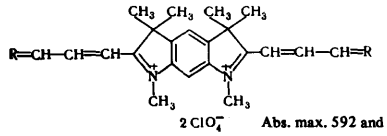


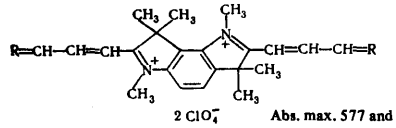
Figure 24.

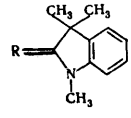
The chromophores in (LIII) lie in opposite directions (cf. preceding footnote §). This is apparent in the spectrum (Fig. 24) as an intense long-wavelength band and a weakly defined short-wavelength band. Two methyl groups introduced into positions 2 and 3 in the benzene ring (bishemicyanine LIV) reduce this angle almost to a right-angle (two maxima of almost equal intensity).

We have already noted—dyes (XXXI) and (XLIII)—that spectral interaction of two chromophores is observed when they are linked not only through the *ortho*- and *para*-positions of a benzene ring but also through the *meta*-position. A special investigation has been made of this last case[49]. Three symmetrical biscyanines (LV)–(LVII)



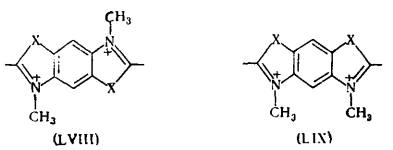






were prepared from isomeric dimethyldiazaindacene derivatives. Mutual separation of the absorption bands is observed with all three bis-dyes, but its value Δ, representing the degree of interaction of the combined chromophores, is 139 nm in (LV), in which the chromophoric chains are conjugated through the *para*-position of the benzene ring, whereas it is 77 and 74 nm, i.e. only half, in the biscyanines (LVI) and (LVII), where the same chains are combined through the *meta*-position.

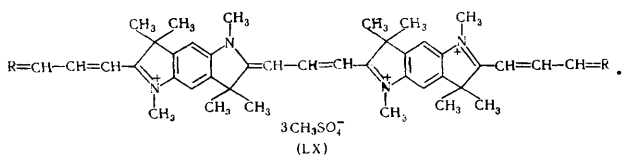
In the analogous biscyanines containing fused thiazolobenzothiazole or oxazolobenzoxazole rings as central nucleus the structures (LVIII) and (LIX)



(LVIII) (LIX)

(where X = S, O) show little difference in mutual separation of the bands. In these dyes, however, conjugation can be accomplished not only through the nitrogen atoms but also through the sulphur or oxygen atoms.

In concluding this survey we note that it has recently proved possible[50] to synthesise the first triscyanine dye (LX)



(LX)

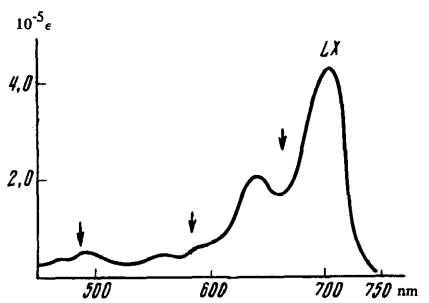


Figure 25.

Fig. 25 shows that the absorption curve of this dye in nitromethane contains bands corresponding to three electronic transitions (indicated by arrows).

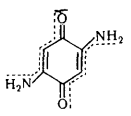
From all that has been stated concerning the interaction of conjugated chromophores it must be concluded that a cautious approach is necessary to the use of spectral methods to determine the structure of organic compounds. In the infrared and nuclear magnetic resonance spectra each group of atoms is represented by a band or region of characteristic absorption, so that these methods are extremely valuable for the determination of structure. But the attempts of many chemists to establish such characteristic frequencies in electronic spectra, e.g. for substituents in aromatic and heterocyclic ring systems, have been unsuccessful. For the most part conjugated chromophores do not absorb at all in the spectral region in which the isolated chromophores absorb. It was therefore supposed that on conjugation the individual chromophores merge into a single longer chromophore, which absorbs at longer wavelengths. We now know that the situation is more complicated, and that the conjugation of two chromophores results in the formation of two new absorption bands, for each of which both interacting chromophores are responsible.

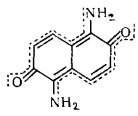
This interaction of chromophores has been discussed in the quantum theory of the spectra of organic compounds[16,51]. The probable reason why it has not been observed hitherto in the spectra of simple conjugated systems, e.g. the absorption spectra of aromatic hydrocarbons and polyenes, is that such spectra are too complicated, consisting of a large number of closely spaced bands. However, the splitting of bands has been observed by Davydov in the spectra of molecular crystals of naphthalene and anthracene at low temperatures, when the bands are especially narrow, and has been brilliantly explained by him (Davydov splitting)[52,53]. It must also be borne in mind that, according to London's theory, electrical interaction between oscillators in molecules should be greater the stronger the oscillators and the longer the longest wavelengths of absorption bands due to the molecule. Consequently resonance interactions should be more clearly developed between dye molecules than between aromatic hydrocarbon molecules containing conjugated systems of the same length[54]. Earlier spectroscopic investigations on bisazo-dyes have not resulted in the discovery of splitting of their absorption bands, for the dyes studied mostly had linear molecules, in which splitting should not have been observed. Furthermore—probably the most important reason—the absorption bands of azo-dyes are broad, overlapping, and devoid of distinct maxima. It is not surprising that cyanine dyes, with their narrow and intense absorption bands, provided greater success.

As early as 1944 Förster[55,56] used the interaction of π-electron systems to explain the absorption bands of dimeric cyanine dyes, which lay at shorter wavelengths than the bands due to the monomers. The chromophores were arranged parallel to each other in the molecules of these dimers. Recently Kuhn[57] has shown that, in monomolecular layers of simple cyanine dyes deposited on a glass surface in such a way that the chromophoric chains of two neighbouring molecules A and B are contiguous, the chromophores begin to interact as coupled oscillators. As a result, the absorption band of dye A is displaced in one direction, and that due to dye B in the other, so that the bands move apart.

Whether in Davydov's molecular crystals, in dimers of cyanines, or in Kuhn's monolayers of dyes, the interacting molecules only approach one another, but do not form covalent bonds. Recently, however, Dähne has shown[58] that the deep and intense colour of certain aromatic and heterocyclic compounds, including Indigo Blue, Indanthren Blue, and Alizarin, can be regarded as resulting from the interaction of two electronic oscillators bound covalently into a single cyclic system

(coupling effect). This has been shown especially convincingly for red 2,5-diamino-*p*-benzoquinone (LXI) and blue 1,5-diamino-2,6-naphthaquinone (LXII)





336 and 488 nm 321 and 581 nm

Absorption maxima in $(CH_3)_2SO$

(LXI) (LXII)

which, according to Dähne, are doubly bound merocyanine molecules. This has been confirmed by appropriate quantum-mechanical calculations of the absorption maxima of these compounds, investigation of their ultraviolet and nuclear magnetic resonance spectra, and X-ray examination of the crystals [59-61].

Nevertheless, as is evident from the present review, it is only by investigating the spectra of bis-dyes in which the two component dye molecules are combined into a single open conjugated chain that we were able to establish that not all combined chromophoric systems interact spectroscopically, but only those which absorb similar quanta of light energy, that the intensities of the two absorption bands of a bis-dye can be used to estimate the direction of its chromophores in space, that these directions are easily changed by steric and electronic factors, etc.

The investigation of bis-dyes having conjugated chromophores has opened a new chapter in the theory of colour and constitution.

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Thermochemical Constants of $A^{III}B^{V}$ Compound Semiconductors, and Approximate Methods of Calculation

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Published data on the phase diagrams and on the nature of melts in the A^{III}–B^{V} system and on the thermochemical constants of $A^{III}B^{V}$ semiconducting compounds are reviewed. Approximate methods of calculating thermochemical constants are suggested: they are based on summing the constants of the elemental semiconductors whose atomic weights add up to the molecular weight of the compound. 128 references.

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I. INTRODUCTION

$A^{III}B^{V}$ compounds, composed of elements of Groups III and V of the Periodic Table, have recently attracted a great deal of attention from physicists, chemists, and device technologists because of their semiconductor properties [1]. The properties of $A^{III}B^{V}$ compounds have increased our understanding of semiconductors, and have given rise to new applications in different branches of electronics: in semiconductor electronics (by virtue of the properties of their crystal lattice), in molecular electronics (by making possible new solid-state circuits), and in quantum electronics (which relies on quantum phenomena within the atoms and molecules of the material).

A knowledge of the thermochemical properties of $A^{III}B^{V}$ compounds (or III–V compounds) is essential to the full understanding of their nature and properties, and also for the development of apparatus and techniques for preparing these compounds and for producing devices from them. The constants which must be known to solve the first problem include the enthalpy and entropy of formation of the compound, the free energy of the formation reaction, the heat of atomisation, the absolute entropy, etc. The second and the third problem cannot be solved without a knowledge of the phase diagrams of the individual components and of the compound, of the vapour pressure of the volatile component at the melting point, of the specific heat, heat of melting, etc.

Many of the above constants have been determined experimentally for the compounds which can be prepared relatively easily. Some of these compounds, however, have high melting points and high vapour pressures of the volatile component at their melting point: most of the physicochemical constants which are available for these compounds were obtained by calculation and are only tentative. In many cases data are altogether lacking.

This review attempts to systematise the thermochemistry of III–V compounds by a critical discussion of published methods of evaluating physicochemical constants by approximate calculations.

II. PHASE DIAGRAMS AND NATURE OF MELTS IN A^{III}–B^{V} SYSTEMS

With the exception of boron-containing systems, the phase diagrams of A^{III}–B^{V} systems (plotted as T against x, where T is temperature and x is the composition in at.%) are all of the same type [2]. They all include one congruently melting compound (of 1:1 atomic composition) whose melting point is much higher than the melting points of the components (Fig. 1). The eutectic on the side of the A^{III} component is degenerate. The other eutectic, on the right-hand side of the diagram, usually lies at high concentrations of the B^{V} component. An analysis of these phase diagrams suggests that only the compound can have semiconductor properties in these binary systems.

As the atomic weight of the component atoms increases, the shape of the phase diagram for the binary system changes, indicating a change in the type of interaction between the elements. In the heaviest systems the phase diagrams no longer show a 1:1 compound (see, for example, the rare earth element–bismuth systems). The new compounds have neither a tetrahedral structure nor semiconductor properties.

The semiconducting phases in the binary systems belong to the type known as linear phases, in which the solubility of the components is very low. Mironov and Borisova [15] have discussed deviations from stoichiometry in the III–V semiconductors and the methods used to study these deviations.

Thermodynamic arguments based on the free-energy curves for the crystal and the melt in a binary system which forms a compound semiconductor have shown that the maximum melting point (the distectic point) of the compound does not coincide with the stoichiometric composition. The phase diagram of the binary system in the region of the compound takes the form shown in Fig. 2. Crystals grown from a melt lying in the composition region *3* contain an excess of component B, those grown from region *1* contain an excess of component A. A crystal of exactly stoichiometric composition can be grown only from a melt of composition *Q*.

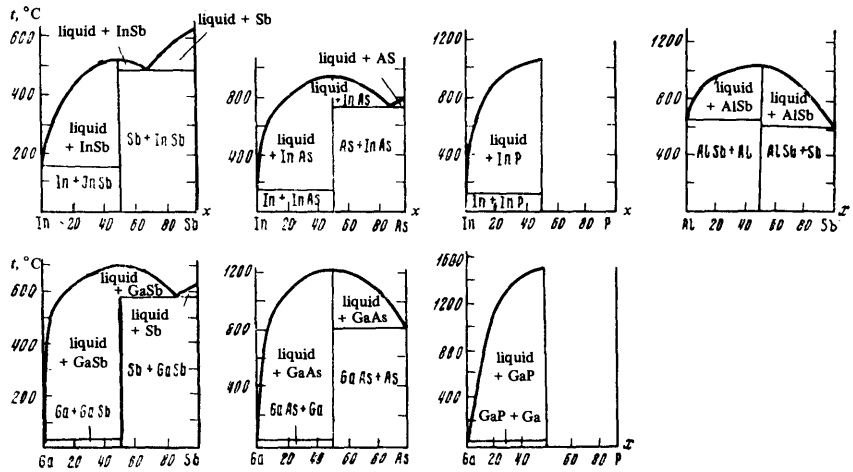

Figure 1. Phase diagrams of some $A^{III}-B^{V}$ systems in $T-x$ coordinates: In–Sb,[3,4] In–As,[5,6] In–P,[6,7] Al–Sb,[8,9] Ga–Sb,[10,11] Ga–As,[6,11] Ga–P.[12,14]

However, in most III–V compounds the deviations from stoichiometry arising from the solubility of an excess of the components in the compound are not detectable by precision X-ray, chemical, or mass-spectroscopic analyses. $A^{III}B^{V}$ semiconductors can be prepared with such a low concentration of current carriers (under conditions leading to mutual compensation of impurities and native defects) that the presence of a stoichiometric excess of one of the components is inconceivable. GaAs and GaSb are exceptional in this respect: a shift of their maximum melting point towards the gallium-rich side has been detected by an indirect method [16,17].

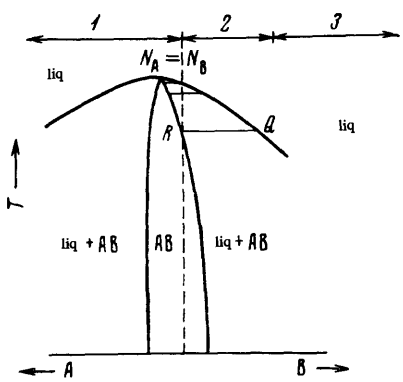

Figure 2. Part of the phase diagram in the region of the compound semiconductor, illustrating the deviation of the maximum melting point from the stoichiometric composition [15].

The most likely source of deviations from stoichiometry in III–V compounds are lattice defects and impurity atoms. The latter can displace normal atoms from lattice sites or, if they are not too large, they can reside in interstitial sites. In either case, the conductivity type of the compound is affected. Atom displacements (or substitutions) in the lattice of a III–V compound can produce point defects of various types: vacancies at the normal lattice sites, interstitial atoms surrounded by four atoms of the same kind or of the opposite kind, and the substitution of atoms of one kind by atoms of the other kind [18].

These structural defects appear to be the only mechanism by which the composition of III–V compounds can deviate from stoichiometry. Many attempts at inducing non-stoichiometry by adding an excess of one of the components to the melt, by diffusion of the vapour of the volatile component into the solid compound, or by other methods, were unsuccessful. The conclusion, which is extremely important in the technology of III–V compounds, is that small variations in the composition of the melts used to grow single crystals of the compounds have a negligible effect on the physical properties of the crystals.

Equilibrium in the A–B systems involves four phases: component A(sol), component B(vap), a solution of component A(liq) in B(liq), and the compound AB(sol). This equilibrium corresponds to a quaternary point in the $p-T-x$ diagram (where p is pressure) at the intersection of four lines characterising the corresponding three-phase equilibria [19]. In unstable III–V compounds the quaternary point lies in the region of low pressures, at temperatures close to the melting point of component A, and consequently at low concentrations of component B in solution.

An analysis of all possible phase equilibria indicates that, for all practical purposes, the most important equilibrium is

$$AB(sol) \rightleftharpoons \text{solution of B in A(liq)} \rightleftharpoons B(vap) \ .$$

Three-phase equilibria in binary systems are monovariant ($v = 3$, $F = 1$). Hence, this equilibrium is described on a $p-T-x$ diagram by a curve terminated at one end by the quadruple point and at the other end in one of a number of ways [20,21], depending on the type of interaction between the components A and B.

The binary phase diagram for an involatile (A) and a volatile (B) component which react to give a semiconducting

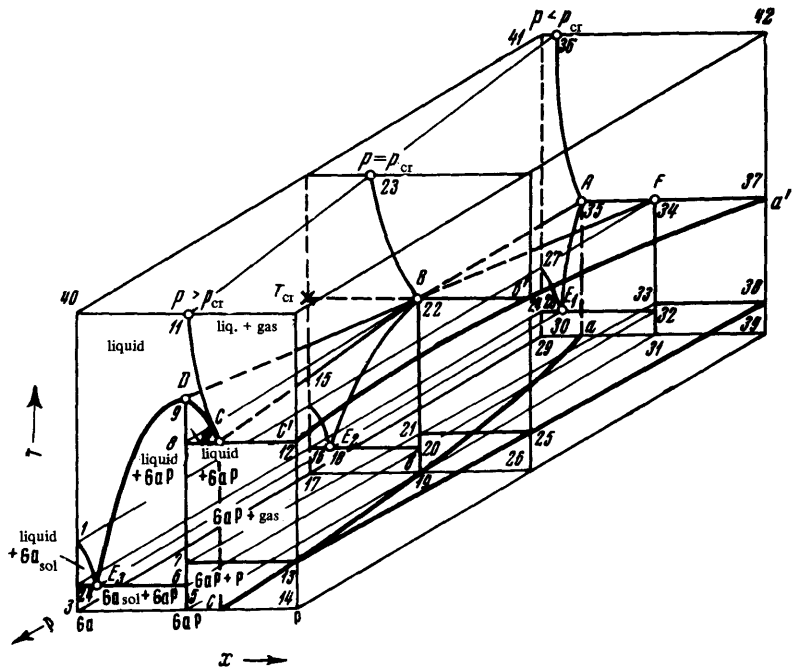

Figure 3. Hypothetical three-dimensional phase diagram for the gallium–phosphorus system [12].

compound at low pressures is of the peritectic type. Unstable compound semiconductors are almost completely dissociated below the melting point when heated under normal conditions, and therefore their liquidus curve does not show a maximum.

However, when the pressure is raised, the regions of the phase diagram are displaced towards the point where the liquid phase composition is the same as that of the compound, and the solid phase begins to take part in the transformations [22,23]. On further raising the pressure the peritectic phase diagram is converted into a phase diagram with a normal maximum [24].

The transition from one type of phase diagram to the other under the influence of external pressure is illustrated by the hypothetical three-dimensional phase diagram for the Ga–GaP system shown in Fig. 3. The diagram includes the following regions and equilibrium lines:

Two-phase regions: *1–2–3–18–30–27–28–16–15–1* (melt + Ga crystals); *2–3–5–6–20–16–17–19–31–32–28–29* (GaP crystals + Ga crystals); *5–7–13–14–26–19–21–25–38–39–31–32* (GaP crystals + P crystals); *6–4–9–6–20–32–34–22–35–30–18–4* (melt + GaP crystals); *9–22–10–8* (melt + GaP crystals).

Single-phase region: *40–41–36–28–11–10–9–41–27–30–35–36* (melt).

Two-phase equilibrium lines: *BD* (GaP crystals + melt); *a′b′c′* gives the temperature variation of the vapour pressure of liquid P; *1–15–27* gives the pressure dependence of the melting point of Ga; *13–25–38* gives the temperature dependence of the vapour pressure of solid P.

Three-phase equilibrium lines: *ABC* (melt + GaP crystals + vapour); $E_1E_2E_3$ (melt + GaP crystals + P crystals); *BF* (melt + GaP crystals + vapour). *B* is the point corresponding to the four-phase equilibrium (melt + GaP crystals + liquid P + P vapour).

The three-phase equilibrium of interest (compound AB(sol)–solution of component B in A(liq)–component B(vap)) is shown by the line *CBA* in the three-dimensional diagram (see Fig. 3). The projections of this line are shown on the three coordinate planes: *cba* on plane p–x, $c'b'a'$ on plane p–T, and E_3D on plane T–x.

Fig. 4 shows a series of consecutive isobaric sections of the three-dimensional phase diagram, drawn by Folberth [25] to demonstrate the shift of the point representing the three-phase equilibrium line on the T–x plane (points *1–5* in Fig. 4*a*–4*e*) caused by an increase of pressure. The point goes through a maximum (Fig. 4*f*).

Wagner [26] has discussed the general case of equilibrium between liquid and solid phases in a binary system containing a compound. The liquidus curve (Eqn. (1)) was derived without making allowance for the temperature dependence of the energy of mixing ω ($\omega = \omega_{AB} - (\omega_{AA} + \omega_{BB})/2$, where ω_{AB}, ω_{AA}, and ω_{BB} are the interaction energies between unlike and like atoms) or for the difference in specific heat between the solid and the liquid phase of the compound:

$$\omega = \frac{RT}{2(x-0.5)^2}\left[\ln\frac{1}{4x(1-x)} - \frac{\Delta S_f}{R}\left(\frac{T_f}{T}-1\right)\right], \qquad (1)$$

where ΔS_f and T_f are the entropy and the temperature of fusion of the compound, x is the atom fraction of component B in the melt, and R is the gas constant.

Eqn. (1) was applied to InSb and GaSb by Schottky and Bever [27], who postulated that melts of these compounds are regular solutions with an entropy of melting equal to the ideal entropy of mixing. Experimentally, gallium antimonide melts were found to behave like ideal solutions whereas indium antimonide melts gave negative deviations from ideality.

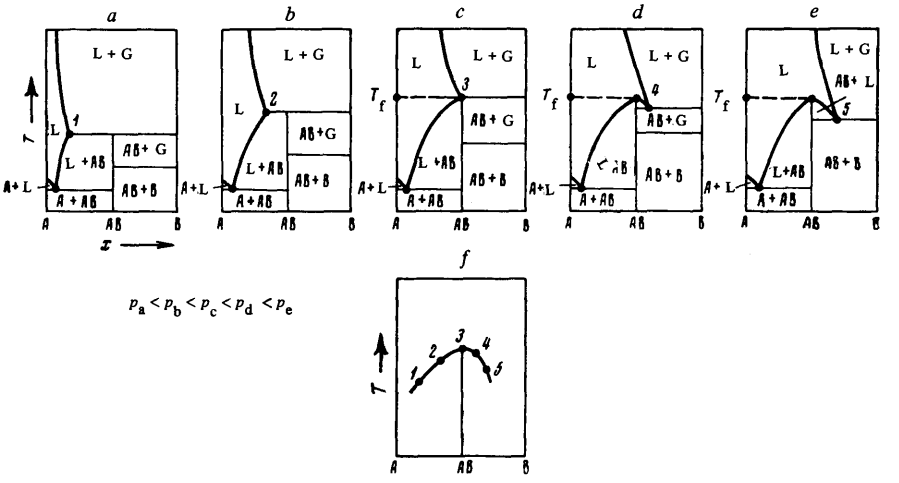

Figure 4. Isobaric sections of the phase diagram for a binary system consisting of an involatile component A and a volatile component B and forming a semiconducting compound AB: *a*)–*e*) isobaric sections; *f*) projections of the three-phase equilibrium point (AB_{sol}–solution of B in Aliq–B_{gas}) on the T–x plane (liquidus line).[25]

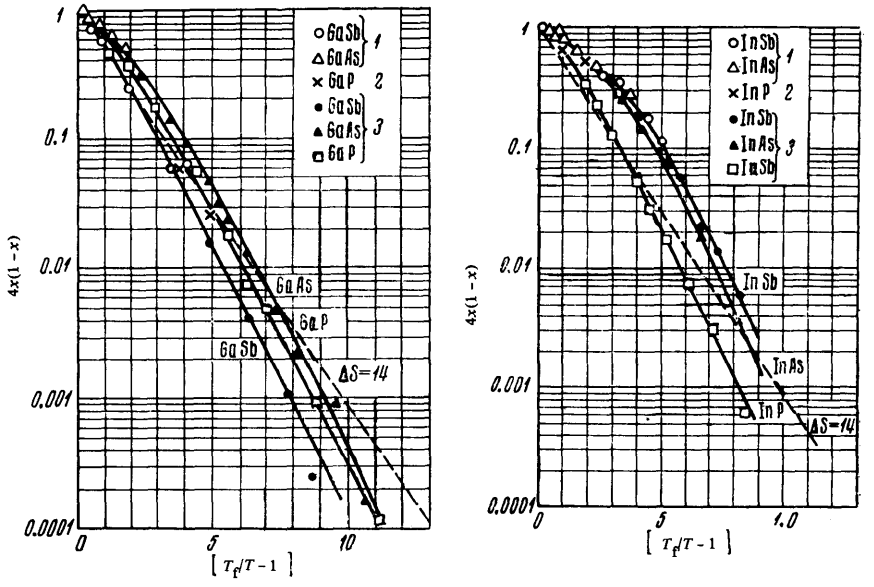

Figure 5. Dimensionless plots of the solubility of GaSb, GaAs, GaP, InSb, InAs, and InP: *1*) after Ref. 11; *2*) after Ref. 14; *3*) after Ref. 13.

Wieland[28] used regular solution theory to interpret data on the vapour pressure of III–V compounds:

$$p^{1/4} = p_0^{1/4} \cdot \exp[\omega(1-x)^2/RT] \text{ atm}, \quad (2)$$

where p is the pressure of tetra-atomic molecules of the volatile component B^V over a melt of A^{III} containing an atom fraction x of component B, and p_0 is the pressure of the same molecules over the pure liquid component B at the given temperature. In practice, Eqn. (2) is difficult to apply to the determination of the equilibrium pressure of component B over melts of approximately stoichiometric composition because of the lack of reliable vapour pressure data for the pure liquid components B (such as phosphorus, arsenic, etc.) whose vapour pressure is high at high temperatures.

According to Hall[13], $A^{III}B^V$ melts behave as ideal solutions at low temperatures. In this case $\omega = 0$, and plots of $\ln 4x(1-x)$ against $(T_f/T - 1)$ are linear for all systems, with a slope of $\Delta S_f/R$. All the plots are found to have approximately the same slope (Fig. 5), corresponding to an entropy of fusion of $\Delta S_f^* = 14$ cal mole^{-1} deg^{-1} for the ideal solution.

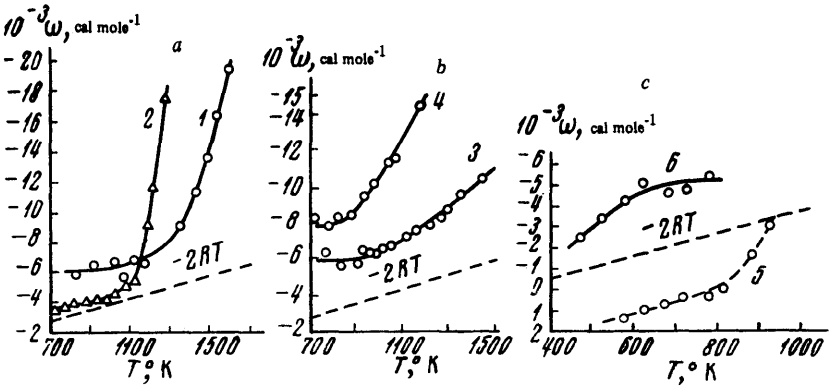

Figure 6. Variation of the energy of mixing with temperature, calculated from experimental liquidus data for A^{III}–B^{V} systems [29,30]: *1*) Ga–P, *2*) In–P, *3*) Ga–As, *4*) In–As, *5*) Ga–Sb, *6*) In–Sb.

A thermodynamic analysis of the liquidus curves for the systems formed by gallium and indium with phosphorus, arsenic, and antimony, based on Eqn. (1), has yielded the energies of mixing of those systems [29,30]. The values (Fig. 6) were found to be a function of temperature and of the concentration of the melt: hence, these systems cannot be treated as regular solutions. In all systems the energy of mixing tends towards zero as the concentration of the Group V element decreases. With the exception of the Ga–Sb system, the calculated energies of mixing are smaller than $-2RT$, pointing to a strong interaction between unlike atoms and confirming the theoretical conclusion of Pines and Kamenetskaya [31,32] that compound formation should occur in systems for which $\omega < -2RT$.

The Ga–Sb system differs from all the others [30] in having an energy of mixing more positive than $-2RT$ over the whole range of temperatures (see Fig. 6*c*), and therefore also of compositions: its value lies in the range 0–2 kcal mole^{-1}. This observation lends support to Schottky and Bever's statement [27] that gallium–antimony melts can be treated as ideal solutions. The bond in liquid gallium antimonide has a greater proportion of metallic character than in any other III–V compound [33]. This phenomenon may be responsible for the anomalous thermodynamic properties of the material.

The temperature dependence of the energy of mixing obtained in the above work [29,30] is inconsistent with the results of Thurmond [34], who found a linear dependence for the Ga—As and Ga—P systems, the quantity ω changing sign as it passes through zero. This may be due to an incorrect choice of entropies of melting by Thurmond [34]: there is serious disagreement on the entropies of melting of GaAs and GaP among different workers.

III. TEMPERATURE, HEAT, AND ENTROPY OF MELTING

The melting points of most of the antimonides and arsenides are quite accurately known; conflicting data have been published for some of the phosphides, and the values for most of the nitrides are purely tentative.

The melting points of the III–V semiconductor compounds, listed in Table 1, show a correlation with the position of the components in the Periodic Table. The melting points of the compounds decrease as the molecular weight increases. Vigdorovich and coworkers [47] have pointed out that the rule [48,49], according to which the melting points of elements with a covalent type of bond increases as the shortest interatomic distance in the crystal lattice decreases, applies also to III–V compounds (see Fig. 7). Only aluminium and gallium antimonides fall outside the linear relationship.

Table 1. Melting points (°C) of III–V compounds.

A^{III}	B^{V} N	Ref.	P	Ref.	As	Ref.	Sb	Ref.
B	~3000*	35	~2500	35	~2000	35	—	
Al	~2200***	36	>1800	37	>1700	38	1065	39
							1080	36
Ga	~1300***	40	>1350	41	1237**	6	703	11
			1522**	42				
			1500—1550	43			712	46
			1467**	14				
In	~1200		1062**	10	943**	4		
			1045	11			536	3
			1058**	44			525	11
			1055**	45				

*Cubic modification; **under equilibrium vapour pressure of the volatile component; ***under 4 atm nitrogen pressure.

In most cases, the thermodynamic characteristics of the melting of III–V compounds have been obtained by indirect calculations. Experimental and calculated values of the heat and entropy of melting of semiconductor compounds are given in Tables 2 and 4.

Glazov and Krestovnikov [50] measured the heat of melting of a number of III–V compounds, and showed that this parameter decreases when the cation or the anion are replaced by a heavier atom, in the following sequence: AlSb → GaSb → InSb and GaAs → InAs.

Melekh and Semenkovich [51] proposed an approximate method of calculating the entropies and heats of melting of compound semiconductors, based on the formula [36]

$$\Delta S_f = \sum S_{f,el.} + S_{mix}, \qquad (3)$$

where ΔS_f is the entropy of fusion of the alloy, $S_{f,el}$ is the entropy of fusion of the constituent elements, and S_{mix}

is the entropy of mixing of the alloy, calculated from the formula

$$S_{mix} = R(N_1 \cdot \ln N_1 + N_2 \cdot \ln N_2)$$

where R is the gas constant and N_1 and N_2 are the atom fractions of the elements in the binary alloy.

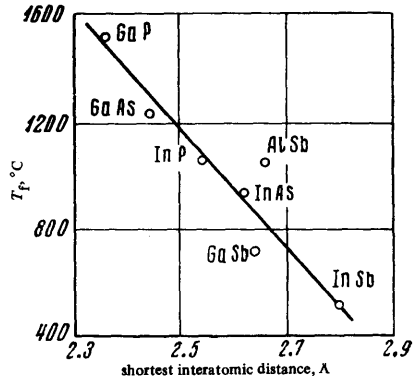

Figure 7. Melting point of some III–V compounds as a function of the shortest A^{III}–B^{V} distance in the crystal lattice [49].

Table 2. Experimental and calculated heats of fusion (kcal mole^{-1}) of some III–V compounds.

A^{III}	B^{V} P	Ref.	As	Ref.	Sb	Ref.
Al	—	—	—	—	14.2	52
					14.7	36
					14.5	51*
Ga	29.2	13	21.0	54		
	28.6	53	23.2	55	12.0	27.51
	30.7	12	20.6	51*		
In	11.0	10	12.6	56	9.0	54
	15.2	11	14.4	28	7.6	4
	12.0	54	12.9	51*	7.9	51*

*Calculated.

The same workers [51] have shown that the approximate calculation of ΔS_f by formula (3) is justified if the behaviour of the compound semiconductor at the melting point is of the semiconductor–metal type (III–V compounds, germanium, silicon, etc.). If, on the other hand, the behaviour is of the semiconductor–semiconductor type (tellurides, selenides, etc.), the term for the entropy of mixing should be omitted in formula (3). Conversely, a good agreement between the experimentally determined value of ΔS_f for a compound semiconductor and the value given by formula (3) is a convincing argument for assigning the compound to the semiconductor–metal melting type (in which a completely disordered solution is formed in the liquid state, with considerable weakening of the chemical bond). An experimental value much lower than the value given by formula (3) indicates melting of the semiconductor–semiconductor type.

It was pointed out above, in the discussion of the phase diagrams of A^{III}–B^{V} systems, that the interaction between the constituent elements of the compound depends on the atomic weight of the elements. III–V compounds and Group IV elemental semiconductors are isoelectronic analogues: they belong to the same crystal-chemical group of diamond-like semiconductors and they have similar bond types and energy spectra. Hence, many thermochemical constants of the III–V compounds can be evaluated by summing the constants for the elemental semiconductors whose atomic weights add up approximately to the molecular weight of the compound semiconductor.

Table 3. Molecular weights of III–V compounds and corresponding sums of the atomic weights of elemental Group IV semiconductors.

III–V compounds		Elemental semiconductors	
Formula	Molecular weight	Elements	Sum of atomic weights
BN	24.8	2C	24.0
AlN	40.98	C+Si	40.1
GaN	83.72	C+Ge	84.6
InN	128.76	C+α-Sn	130.7
BP	41 82	Si+C	40.1
AlP	57.98	2Si	56.18
GaP	100.7	Si+Ge	100.7
InP	145.7	2Ge	145.2
BAs	85.3	Ge+C	84.6
AlAs	101.9	Ge+Si	100.7
GaAs	144.6	2Ge	145.2
InAs	189.7	Ge+α-Sn	191.3
BSb	132.6	α-Sn+C	130.7
AlSb	148.7	α-Sn+Si	146.8
GaSb	191.4	α-Sn+Ge	191.3
InSb	236.4	2α—Sn	237.4

The molecular weights of the III–V compound semiconductors and the sums of the atomic weights of their corresponding elemental semiconductors from Group IV of the Periodic Table are listed in Table 3.

Table 4. Experimental and calculated entropies of melting (cal mole^{-1} deg^{-1}) of III–V compounds.

A^{III}	B^{V} P	Ref.	As	Ref.	Sb	Ref.
Al	14.4*		13.78*		10.8	52
					10.5	36
					10.7**	
					12.4*	
Ga	16.8	13	14.9	55	12.2	27
	17.0	12	14.0	34	12.5**	
	15.0	34	13.6	54	11.78*	
	13.78*		13.3			
			13.16**			
In	8.2	10	10.4	56	11.2	54
	11.4	11	11.8	28	9.5	4
	13.6*		10.7**		9.8	
			11.78*		10.4*	

*Calculated by adding the entropies of melting of the elemental semiconductors.
**Calculated by the method of Melekh and Semenkovich [51].

Table 4 gives the experimental and the calculated entropies of melting of the III–V compound semiconductors. The calculated values were obtained either by adding the entropies of melting of the appropriate elemental semiconductors or by means of Eqn. (3). [51]

IV. STANDARD ENTROPY

Very few data on the entropy and other thermochemical constants of III–V compounds have been published, and most of the published values are computed.

Table 5. Absolute standard entropies of Group III and V elements of the Periodic Table (cal mole^{-1} deg^{-1}), after Kubaschewski and Evans [36].

Element	S^0_{298}	Element	S^0_{298}
$B_{(sol)}$	1.07	$As_{(sol)}$	8.40
$Al_{(sol)}$	6.77	$Sb_{(sol)}$	10.50
$Ga_{(sol)}$	9.80	$C_{(sol)}$	1.36
$In_{(sol)}$	13.98	$Si_{(sol)}$	4.53
$N_{2(g)}$	22.80	$Ge_{(sol)}$	7.43
$P_{(sol)}$	10.60	α-$S_{(sol)}$	10.46

The method of calculating standard entropies for III–V compounds is described by Kubaschewski and Evans [36], who deal particularly with AlN, AlSb, and GaN. Their calculation is based on experimental data on equilibrium constants and on heats of formation, and also on the standard entropies of the component elements (Table 5).

Table 6. Shortest distances (Å) between atoms in III–V compound semiconductor lattices of the sphalerite type [18].

A^{III}	B^V			
	N	P	As	Sb
B	1.58	1.97	2.06	—
Al	—	2.36	2.43	2.64
Ga	—	2.36	2.44	2.66
In	—	2.54	2.62	2.80

They use the equations

$$\Delta G^0_{298} = -298\,R\ln K_p \qquad (4)$$

$$\Delta S^0_{298} = {}^1/_{298}(\Delta H^0_{298} - \Delta G^0_{298}) \qquad (5)$$

$$S^0_{298} = \Delta S^0_{298}(A^{III}B^V) + S^0_{298}(A^{III}) + S^0_{298}(B^V), \qquad (6)$$

where ΔG°_{298} is the free energy of formation of the compound, ΔH°_{298} is the enthalpy of formation of the compound, ΔS°_{298} is the entropy of formation, and S°_{298}, $S^\circ_{298}(A^{III})$, $S^\circ_{298}(B^V)$ are the standard entropies of the compound and of the constituent elements. R is the gas constant and K_p is the equilibrium constant of the formation reaction at pressure p.

The standard absolute entropies of III–V compounds can be calculated also from X-ray diffraction data. Renner [40] evaluated the entropies of inorganic compounds by means of the formula [57]

$$S^0_{298} = 1.5\,R\ln A + R\ln V - 1.5\,R\ln T_f + 12.5 \qquad (7)$$

where S°_{298} is the mean atomic entropy (cal mole^{-1} deg^{-1}), A is the mean atomic weight of the compound, T_f is the melting point of the compound (deg K), V is the mean atomic volume, which can be equated to a^3 (where a is the lattice constant, see Table 7). In the case of III–V compounds, Renner [40] subtracts a correction of 5 cal mole^{-1} deg^{-1} from the value given by Eqn. (7).

Table 7. Lattice constants (Å) of III–V compounds crystallising in the sphalerite structure.

A^{III}	B^V							
	N	Ref.	P	Ref.	As	Ref.	Sb	Ref.
B	3.615	35	4.537	59	4.777	60	—	
Al	—		5.451		5.620		6.095	
Ga	—		5.450	60	5.653	61	6.140	62
In	—		5.869		6.058	61	6.479	

The lattice constants of III–V compound semiconductors which crystallise in the sphalerite structure can be calculated [58] by multiplying the shortest interatomic distance (Table 6) by the conversion factor [18] 2.31. The values obtained in this way (no literature reference) are compared in Table 7 with the experimentally determined lattice constants of the III–V compounds.

Table 8. Standard absolute entropies of III–V compounds (cal mole^{-1} deg^{-1}).

Compound	Experimental value	Ref.	Calc. by adding the entropies of the elemental semiconductors*		Calc. from Eqn.(7), with negative correction of 5 cal mole^{-1} deg^{-1}**	
			Value	Discrepancy from experiment	Value	Discrepancy from experiment
BN	3,67	36	2.72	—0,95		—
AlN	5.0	36	5.89	+0,89		—
GaN	8,4	63	8.79	+0,39		—
InN	10.2	64	11.82	+1,62		—
BP	—		5.89	—		—
AlP	—		9.09	—		—
GaP	12.4	66	11.96	—0,44	11,14	—1.26
InP	14.28	65	14.86	+0,58	16.04	+1.76
BAs	—		8,79	—		—
AlAs	—		11.96	—		—
GaAs	15.34	65	14.86	—0.48	15,23	—0.11
InAs	18.10	65	17.89	—0,2	18,88	+0.78
BSb	—	—	12,82	—	—	—
AlSb	15.36	65	14.99	—0.37	16,57	+1.21
GaSb	18.18	65	17.89	—0.29	19.06	+0.88
InSb	20.60	65	20.92	+0.32	23.2	+2.60

*Calculated from data of Tables 3 and 5.
**Calculated from data of Table 7.
The melting points assumed in the calculations are: GaP, 1795; InP, 1330; GaAs, 1510; InAs, 1216; AlSb, 1343; GaSb, 976; InSb, 798°K.

We have calculated the standard absolute entropies of III–V compounds by adding the standard absolute entropies of the appropriate Group IV semiconductors, and we have obtained satisfactory agreement with experimental data. As Table 8 shows, the agreement is better than can be achieved using Eqn. (7).

V. SPECIFIC HEAT

Experimental measurements of specific heat are available only for a few III–V compounds. Thus, Kochetkova and Rezukhina [67] obtained the specific heat of GaSb between 20 and 700° by calorimetric measurements.

Table 9. Specific heat equations of III–V compounds (cal mole^{-1} deg^{-1}) calculated from data obtained from Eqns. (8)–(10).

A^{III}	B^{V}			
	N	P	As	Sb
Al	—	—	$9.004+3\cdot10^{-3}T$	$10.310+4\cdot10^{-3}T$
Ga	$8.122+3\cdot10^{-3}T$	$10.180+2.47\cdot10^{-3}T$*	$10.028+3\cdot10^{-3}T$	$10.668+4\cdot10^{-3}T$
In	$9.863+3\cdot10^{-3}T$	$10.180+4\cdot10^{-3}T$	$10.530+4\cdot10^{-3}T$	$11.804+2\cdot10^{-3}T$

*A correction [73] has been applied to the equation previously accepted [42,47].

Nachtrieb and Clement [68], using a similar method, obtained the following values for the mean specific heat of InSb: 0.052, 0.056, 0.062, 0.062 cal g^{-1} deg^{-1} (or 12.3, 13.2, 14.7, 14.7 cal mole^{-1} deg^{-1}) for the temperature intervals 20–90, 90–170, 170–350, and 350–500° respectively. The low-temperature specific heats of GaP and InP have been measured [66] between 40 and 300°K. Piesbergen [69] determined the temperature dependence of the specific heat of a number of III–V compound semiconductors from data on their Debye characteristic temperature. High-temperature thermodynamic quantities are difficult to calculate, because of the lack of adequate specific heat data. Hence, approximate methods of computation of the specific heat of III–V compounds are very valuable.

Table 10. Specific heat equations for Group IV semiconductors [74].

Element	Specific heat equation	Temp. range, °K
α-Sn	$5.05+4.80\cdot10^{-3}T$	273—504
C	$2.162+3.059\cdot10^{-3}T-1.303\cdot10^{5}\cdot T^{-2}$	273—1313
Si	$5.74+0.617\cdot10^{-3}T-1.01\cdot10^{5}T^{-2}$	273—1174
Ge	$5.94+0.90\cdot10^{-3}T-0.59\cdot10^{5}\cdot T^{-2}$	273—713

Attempts to apply the additivity rule to the temperature dependence of the specific heats of the constituent elements have not been successful, because the specific heat equations for the relatively low-melting components [36,57] are not valid at the higher temperatures of interest for high-melting compounds.

If the melting point is known, an equation for the temperature dependence of the specific heat can be obtained by Kelly's method [70], which assumes a linear variation of specific heat between room temperature and the temperature of the first phase transition. In addition, the following assumptions are made:

1. The molecular specific heat of the compound at room temperature is additive in terms of the atomic specific heats, as required by the rule of Dulong and Petit, and equals 12.6 cal mole^{-1} deg^{-1}. [71]

2. The specific heat of the compound at its melting point is 14.5 cal mole^{-1} deg^{-1}, by analogy with the atomic specific heat of many inorganic compounds at their melting point [36].

Table 12. Comparison of experimental and calculated standard specific heats of III–V compound semiconductors (cal mole^{-1} deg^{-1}).

Compound	Experimental value	Ref.	Calc. from the data of Table 9		Cal. from the data of Table 11	
			Value	Discrepancy from experiment	Value	Discrepancy from experiment
BN	5.61	35	—	—	3.21	−2.40
AlN	7.79	36	—	—	6.40	−1.39
GaN	—		—	—	7.15	—
InN	—		—	—	8.08	—
BP	—		—	—	6.40	—
AlP	—		—	—	9.57	—
GaP	10.43	66	10.92	+0.49	10.32	−0.11
InP	11.30	66	11.37	+0.07	11.08	−0.22
BAs	—		—	—	7.15	—
AlAs	—		9.90	—	10.32	—
GaAs	11.05	69	10.92	+0.13	11.08	+0.03
InAs	11.42	69	11.72	+0.30	12.03	+0.61
BSb	—		—	—	8.08	—
AlSb	11.07	75	11.50	+0.43	11.26	+0.19
GaSb	11.38	67	11.88	+0.50	12.02	+0.64
InSb	12.30	68	12.40	+0.10	12.96	+0.66

The precision of Kelly's specific heat equation can be improved by using Landiya's equation

$$C_p=(C_{v,at}+\alpha_{at}T^{3/2})\cdot n, \tag{8}$$

to calculate the specific heat C_p of the compound at constant pressure, where n is the number of atoms in one molecule of the compound, $C_{v,at}$ is the atomic specific heat at constant volume, α_{at} is the atomic thermal expansion coefficient. The quantities $C_{v,at}$ and α_{at} can be calculated by the equations

$$C_{v,at.}=6.6-\frac{a}{b+k(T-b)} \tag{9}$$

and

$$\alpha_{at.}=\frac{1.24}{T_f}(C_{v,at}^{298})^2\cdot10^{-3}, \tag{10}$$

where T_f is the melting point of the compound and $C_{v,at}^{298}$ is the atomic specific heat at constant volume, obtained

Table 11. Specific heat equations for III–V compound semiconductors, obtained by adding the specific heat equations of the elemental Group IV semiconductors.

A^{III}	B^{V}			
	N	P	As	Sb
B	$4.324+6.118\cdot10^{-3}T-2.606\cdot10^{5}T^{-2}$	$7.902+3.676\cdot10^{-3}T-2.313\cdot10^{5}T^{-2}$	$8.102-2.959\cdot10^{-3}T-1.893\cdot10^{5}T^{-2}$	$7.212+7.859\cdot10^{-3}T-1.303\cdot10^{5}T^{-2}$
Al	$7.902+3.676\cdot10^{-3}T-2.313\cdot10^{5}T^{-2}$	$11.480+1.234\cdot10^{-3}T-2.020\cdot10^{5}T^{-2}$	$11.680+1.520\cdot10^{-3}T-1.60\cdot10^{5}T^{-2}$	$10.790+5.417\cdot10^{-3}T-1.010\cdot10^{5}T^{-2}$
Ga	$8.102+3.959\cdot10^{-3}T-1.893\cdot10^{5}T^{-2}$	$11.680+1.52\cdot10^{-3}T-1.60\cdot10^{5}T^{-2}$	$11.880+1.80\cdot10^{-3}T-1.18\cdot10^{5}T^{-2}$	$10.990+5.70\cdot10^{-3}T-0.590\cdot10^{5}T^{-2}$
In	$7.212+7.859\cdot10^{-3}T-1.303\cdot10^{5}T^{-2}$	$9.24+4.54\cdot10^{-3}T$	$10.990+5.70\cdot10^{-3}T-0.59\cdot10^{5}T^{-2}$	$10.10+9.60\cdot10^{-3}T$

from Eqn. (9) by putting $T = 298°K$. The coefficients a, b, and k in Eqn. (9) take the following values for a compound which dissociates with evolution of a volatile component:

$$a = \frac{4400}{S^0_{298}};\quad b = 298;\quad k = \frac{(2200 - 149 \cdot S^0_{298})}{(5070 - 149 \cdot S^0_{298})}$$

The specific heat values calculated for 298°K and T_f are then used to obtain a linear equation for the temperature dependence of the specific heat, valid between 298°K and T_f. The results are summarised in Table 9.

If the thermodynamic data needed to obtain a specific heat equation for III–V compounds as a function of temperature by the above method are not available, the equation can be produced by summing the specific heat equations for the corresponding elemental semiconductors (see Table 3).

The specific heat equations for the elemental semiconductors of Group IV are listed in Table 10: the specific heat equations for III–V compounds deduced from those data are given in Table 11.

As Table 12 shows, the specific heats of III–V compounds calculated by Landiya's method agree satisfactorily with experimental values. Results fully adequate for approximate calculations are obtained also by adding the specific heat equations of the appropriate elemental semiconductors of Group IV (see Table 12).

VI. ENTHALPY AND FREE ENERGY OF FORMATION AND HEAT OF ATOMISATION OF $A^{III}B^{V}$ COMPOUNDS

The enthalpy of formation of a compound is one of its most important parameters, and is related to many of its physicochemical characteristics. Very few experimental determinations of the enthalpy of III–V compounds have been reported, particularly for compounds which tend to dissociate.

The enthalpy of formation of InSb has been determined fairly accurately by tin calorimetry [27,76], by direct fusion [77], by the e.m.f. method, and by fusion in a bomb calorimeter [81,82]. The enthalpy of GaSb has been measured calorimetrically [27] and by the e.m.f. method [80,83].

The enthalpy of dissociating compounds is difficult to measure experimentally. For InAs the problem has been solved using colorimetric [27,80] and mass-spectrometric [84,85] techniques. Values of the enthalpy of formation of GaAs have been obtained from mass-spectrometric experiments [86], from thermochemical studies of transport reactions involving the compound [87], and by the e.m.f. method [80].

The enthalpy of formation of InP has been obtained from the temperature dependence of the dissociation pressure [88,89], mass-spectrometrically [86], and also by fusion [82] and combustion in a bomb calorimeter [90]. The enthalpy of formation of GaP was first determined [91] from the temperature dependence of the dissociation pressure of the compound. Johnston [92] obtained a different value under similar conditions. Data from combustion experiments in a bomb calorimeter have been reported [90]. More recent work on the enthalpy of formation of GaP has relied on the e.m.f. method [93,94] and on calorimetric measurements [95]. The enthalpy of formation of BP has been measured calorimetrically by the reaction between the compound and gaseous F_2 to give BF_3. [96]

Renner [40] computed the enthalpies of formation of III–V compounds from reactions of the type

$$A^{III}_{(liq)} + \frac{1}{n} B^{V}_{n(g)} \rightleftarrows A^{III}B^{V}_{(g)}$$

using published values of the latent heat of fusion, enthalpy of dissociation, and specific heat of the elements [36,57].

The free energies of formation ΔG°_{298} of the compounds can be calculated from their enthalpies ΔH°_{298} and entropies ΔS°_{298} of formation:

$$\Delta G^\circ_{298} = \Delta H^\circ_{298} - T\Delta S^\circ_{298} \text{ kcal mole}^{-1} \qquad (11)$$

Table 13. Enthalpies of formation of III–V compounds, kcal mole^{-1}.

Compound	T, °K	Reactions			
		$A_{sol} + \frac{1}{2}B_{2(g)} = AB_{(sol)}$	$A_{(liq)} + \frac{1}{2}B_{2(g)} = AB_{(sol)}$	$A_{(sol)} + \frac{1}{4}B_{4(g)} = AB_{(sol)}$	$A_{(liq)} + \frac{1}{4}B_{4(g)} = AB_{(sol)}$
BN	298	60.0[97]; 61.0[98]	—	—	—
AlN	298	63.0[97]; 76.5[99]	—	—	—
		75.6±4[100]	—	—	—
GaN	298	25±0.5[101]	—	—	—
InN	298	4.6[101]	—	—	—
$BP_{(cub)}$	298	27.6±1.1 *[96]	—	—	—
		19.9[102];			
		29±2[103]	—	—	—
		59.1±0.8[106]			
AlP	298	27.8[104]	—	—	—
GaP	298	42.75[105]	44.38[73]	32.6±1.5[84]	29.1[90]; 24.4[93]
					29.0[94]; 24.9[95]
	1000	—	43.82[73]	—	—
	1500	—	42.89[73]	—	29.66[73]
InP	298	—	—	—	21.54[90]
	1000	—	30.2[88]	39.4±0.5[86]	25.8[107]; 25.4[88];
			41.5[107]	30.2[40]	26.0±3.6[89]
BAs	298	29.9[104]	—	—	—
AlAs	298	13.4[104]	—	—	—
GaAs	298	39.3[88]	44.4[87]	20.4[86]; 26.3[107]	
		44.6[107]			28.9[87]
				26.3±0.75[84]	22.5[98]
		44.4±1.5[84]	45.0[107]	—	27.0[107]; 22.1[86]
	1000	—	35.0[108]	—	—
	1000–1280	—	41.1[84]; 40.0[107]	—	26.0[84]; 22.5[107]
TnAs	1000	—	39.0±2.5[108]	—	22.0[108]
GaSb	900	—	41.0[84]	—	25.5[84]
InSb	930	—	7.78[81]	—	—

*Calculated from the reaction between BP and F_2.

For a III–V compound whose vapour phase consists almost exclusively of the component B^V, the free energy ΔG°_T at a given temperature can be calculated from the experimentally observed dissociation pressure at the room temperature:

$$\Delta G^\circ_T = -\frac{RT}{x} \ln p_{B_xV} \qquad (12)$$

where p_{B_xV} is the dissociation pressure of the compound at temperature T.

Table 13 lists the enthalpies of formation of III–V compounds, measured experimentally or calculated by Eqns. (11) and (12).

The heat of atomisation is an important parameter which reflects the strength of the chemical bond in a semiconducting compound and therefore shows good correlation with its electrical and thermochemical properties [109,110].

Table 14. Heat of atomisation (kcal mole^{-1}) of A^{III} and B^V elements and of Group IV semiconductors.

Element	ΔH°_{at}	Ref.	Element	ΔH°_{at}	Ref.
$B_{(sol)}$	107.5	119	$As_{(sol)}$	69.0	121
$Al_{(re)}$	75.0	120	$Sb_{(sol)}$	62.0	121
$Ga_{(sol)}$	66.0	120	$Si_{(sol)}$	89.0	120
$In_{(sol)}$	58.2	120	$Ge_{(sol)}$	78.4	119
$N_{(g)}$	113.7	121	$\alpha - Sn_{(sol)}$	70.0	121
$P_{(sol)}$	75.2	120	$C_{(sol)}$	138.0	63

Moser and Pearson [110] have considered three idealised bond formation schemes in III–V compounds. The atoms of elements in the IIIB subgroup have three electrons with an s^2p^1 configuration in their outer unfilled shell. The atoms of elements in the VB subgroup have five electrons with the s^2p^3 configuration. When a covalent bond is formed, the Group V atom gives up one electron to the Group III atom, producing a V^+ and a III^- ion with four valence electrons each. The electrons take up the sp^3 configuration, forming tetrahedral bonds of the diamond type. However, the atoms also experience an electrostatic attraction. In the case of a neutral (atomic) bond [111], all the atoms retain their valence electrons, and the charge on all the atoms is the same. In the case of an ionic bond, three electrons are transferred from the A^{III} to the B^V atom, and III^{3+} and V^{3-} ions with filled spherical shells are formed.

Folberth [25] has shown that the bond in III–V compounds is covalent, with a significant proportion of ionic character. Because of the additional effect of the ionic contribution to the bond, III–V compounds have a higher bond strength than the Group IV elements [10].

Various empirical and theoretical methods of evaluating the degree of ionicity and the effective charges are discussed in review articles by Madelung [113], Hilsum and Rose-Innes [18], and also in papers by Suchet [114] and Syrkin and coworkers [115]. Sirota and coworkers [116–118] have derived the effective charges and the ionic contributions to the bond energies for aluminium, gallium, and indium phosphides, arsenides, and antimonides from electron density maps.

The heat of atomisation $\Delta H^\circ_{at}{}^{AB}$ is the sum of the enthalpy of formation of the compound from its atoms ($\Delta H^\circ_{298}{}^{AB}$) and of the heats of transformation of the components to the gaseous state ($\Delta H^\circ_g{}^{,A}$ and $\Delta H^\circ_g{}^{,B}$):

$$\Delta H^{\circ,AB}_{at.} = \Delta H^{\circ,AB}_{298} + \Delta H^{\circ,A}_{g} + \Delta H^{\circ,B}_{g} \quad . \qquad (13)$$

Since the heat of atomisation is known experimentally to be an insensitive function of temperature [109] and does not need to be reduced to a standard state, it can be evaluated by the additive method used above to calculate various thermochemical constants (latent heat of fusion, entropy, and specific heat): in this case, from a summation of ΔH°_{at} values for the elemental semiconductors. The data required for the calculation are given in Table 14.

Table 15. Heat of atomisation (kcal mole^{-1}) of III–V compounds.

Compound	Experimental		Obtained by adding ΔH°_{at} values for elemental semiconductors		Difference, %
	$-\Delta H^\circ_{298}$; AB	$-\Delta H^\circ_{at}$; AB	Sum of ΔH°_{at} for C, Si, Ge, and α-Sn	$-\Delta H^\circ_{at}$; AB	
BN	60.0[97]	281.2	2C	276.0	−1.8
AlN	63.0[97]	251.7	C + Si	227.0	−9.8
GaN	25.0[101]	204.1	C + Ge	216.4	+5.4
InN	4.6[101]	176.5	C + α-Sn	208.0	+10.8
BP	27.6[98]	210.3	Si + C	228.0	+7.9
AlP	—	—	2 Si	178.0	—
GaP	24.4[94]	165.6	Si + Ge	167.4	+1.1
InP	22.3[107]	155.7	2 Ge	156.8	+0.7
BAs	—	—	Ge + C	216.4	—
AlAs	—	—	Ge + Si	167.4	—
GaAs	17.7[107]	152.7	2 Ge	156.8	+2.6
InAs	14.8[97]	151.0	Ge + α-Sn	148.4	−1.7
BSb	—	—	α-Sn + C	208.0	—
AlSb	—	—	α-Sn + Si	159.4	—
GaSb	9.9[97]	137.9	α-Sn + Ge	148.0	+7.5
InSb	8.2[79]	128.4	2 α-Sn	140.0	+9.0

Experimental and calculated values of the heat of atomisation of III–V compound semiconductors are compared in Table 15. It is evident from this Table that the difference between the experimental values and those calculated additively does not exceed 11%, with a mean deviation of 5.3%. This degree of accuracy is fully adequate for many approximate calculations.

VII. VAPOUR PRESSURE

Reliable data on the vapour pressure of the volatile components over III–V compounds tending to dissociate are essential to the design of rational methods of synthesis and crystal growth for these compounds. The measurement of vapour pressure in these systems has some unusual features.

Phase equilibria in two-component systems are more complex than the corresponding equilibria in one-component systems: hence, it becomes more difficult to measure the saturated vapour pressure p and also to estimate the reliability of the results. For a solid or a liquid sample in equilibrium with the vapour of the volatile component the number of degrees of freedom given by Gibbs' phase rule is two, i.e. $p = f(T, x)$. For solids this conclusion applies at temperatures below the solidus line, for liquids above the liquidus line of the phase diagram. As a special case, the sample can have the stoichiometric composition, and in this case the system is monovariant, i.e. $p = f(T)$.

If a solid sample is heated above the solidus line, or a liquid sample is cooled below the liquidus line, a third phase appears. In a system of this type, for which a detailed analysis was given by Vigdorovich and Nashel'skii [122], the number of degrees of freedom is one, i.e. $p = f(T)$ at $x = \text{const}$ or $p = f(x)$ at $T = \text{const}$. In the special case of a stoichiometric solid and a stoichiometric liquid an additional constraint is present and the system becomes invariant, and a unique vapour pressure of the volatile component can be measured at the melting point.

The gas-phase composition varies from point to point if the temperature of the sample is not uniform, since molecular dissociation processes (under the influence of temperature) and atomic association processes (under the influence of pressure) take place in the gas phase in opposite directions [88]. Hence, calculations by the Mendeleev–Clapeyron equation are difficult to apply, since they involve the molecular weight of the vapour phase. Furthermore, the measurement of vapour pressure for compound semiconductors which undergo dissociation presents a number of experimental difficulties, including the need to work at high temperatures and pressures and the aggressive nature of the vapours and the melts towards most commonly used container materials. Nashel'skii [123] has reviewed experimental methods of measuring the vapour pressure of dissociating semiconductor compounds, including III–V compounds.

If the experimental difficulties prove insurmountable, the vapour pressure of III–V compound semiconductors can be estimated from thermochemical data by means of Eqn. (12), Many workers have carried out calculations of this type [40,42,49,73]. The temperature dependence of the vapour pressure of the volatile component is usually reported in the form of plots of $\lg p_{B_x^V}$ against $1/T$ (Fig. 8), or in the form of an equation of the type

$$\lg p_{B_x^V} = -\frac{A}{T} + B \quad . \qquad (14)$$

Values of the A and B coefficients of Eqn. (14) for arsenides and phosphides are given in Table 16.

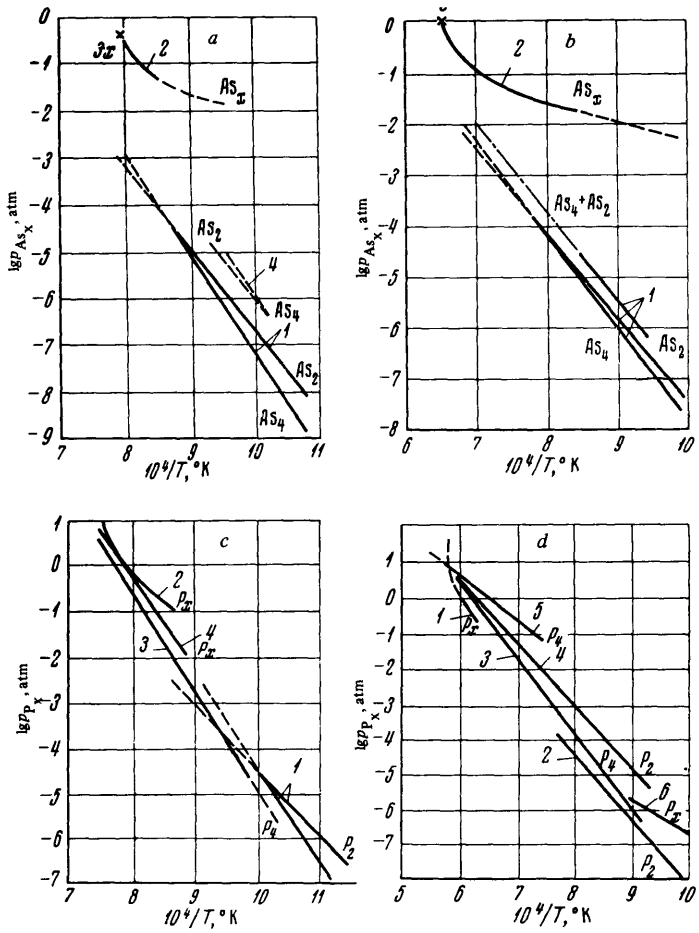

Figure 8. Dissociation pressure of some III–V compounds: (*a*) indium arsenide and (*b*) gallium arsenide [*1*) Ref. 84, 86; *2*) Ref. 44; *3*) equilibrium vapour pressure of arsenic at the melting point of the compound; *4*) Ref. 40]; (*c*) indium phosphide [*1*) Ref. 84, 86; *2*) Ref. 92; *3*) Ref. 44; *4*) Ref. 88, 89]; (*d*) gallium phosphide [*1*) Ref. 44; *2*) Ref. 92; *3*) and *4*) Ref. 73; *5*) Ref. 91; *6*) Ref. 127].

The dissociation pressure of InSb and GaSb is very low [84,86]. The vapour pressure of Sb and InSb over InSb has been measured [125] by an effusion method, with radioactive isotopes. The vapour pressure of Sb over GaSb samples of different composition has been measured [126] by the "dew-point" method.

Table 16. Experimental values of the temperature dependence of the dissociation pressure of III–V arsenides and phosphides (atm).

Compound	Molecular composition of vapour	Numerical values of constants in Eqn.(14)		Temp. range, °K		Equilibrium pressure of the B^V component at the melting point of the compound	
		A	B				
InAs	As_2	18.840	24.00	911—1195	109	0.33	11
	As_4	22.725	27.25				
GaAs	As_2	17.340	9.86	950—1200	109	0.9	11
	As_4	19.320	24.66			~1.0	44
InP	P_2	14.850	10.32	775—900	109	~21	44
		21.300	16.84				
	P_4	23.000	21.00	973—1318	89	~40	88
		19.200	13.80	1123—1243	88		
GaP	P_2	13.650	6.90	973—1073	127	~20	12
		18.870	13.60	1054—1278	92	~35	44
	P_4	12.510	8.167	1350—1678	91		

All the thermochemical data relating to III–V compound semiconductors indicate a gradual variation with the molecular weight of the compound. The lattice parameter, specific heat, and standard entropy increase with molecular weight in an isoelectronic series. Conversely, the melting point, heat of fusion, entropy of fusion, enthalpy of formation, and heat of atomisation decrease with increase of molecular weight in an isoelectronic series.

These changes are consistent with the changes in the nature and strength of the chemical bond [124,128] in III–V compounds expected from the position of their constituent elements in the Periodic Table.

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Liquid Lasers Based on Lanthanide Complexes

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The review deals with the chemical problems concerning the use of neodymium, europium, gadolinium, and terbium complexes in liquid lasers. The equilibria arising in solutions are briefly examined. The principal liquid laser systems have been analysed. The systems can be divided into two types: chelate systems with transfer of absorbed energy from the ligand molecule to the lanthanide ion (these include europium, gadolinium, and terbium complexes) and systems based on neodymium complexes in inorganic solvents. The latter are distinguished by enhanced stability to the action of light and are at present the most promising for the preparation of liquid lasers.
The effect of solvents and structure of the complexes on the laser properties of the systems is also discussed. The bibliography includes 109 references.

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I. INTRODUCTION

The lanthanide elements have been used successfully to make lasers comparatively long ago. So far the laser effect produced by crystals and glasses has been obtained for the following lanthanides: praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, and ytterbium[1-5]. During the last ten years, several multicomponent liquid systems with laser properties were obtained on the basis of lanthanide complexes.

The formation of lasers based on liquid systems constitutes a major and complicated problem in the development of which the work of both physicists and chemists is combined. Advances in studies in this field depend entirely on their joint efforts. Some of the problems can be solved by physicists and others by chemists.

The first class of problems, which are in principle solved by physicists and therefore may be arbitrarily called "physical", may be said to include problems such as the methods for the design of lasers under different operating conditions, a number of experimental and theoretical problems concerning the development and formation of active media based on organic and inorganic materials, and the choice of resonators, optical pumping systems, and optical shutters.

Usually physicists investigate the fundamental characteristics of lasers: the pumping rate, emission intensity, efficiency, and also the spectroscopic and time characteristics of laser emission. The study of the angular divergence of the emission plays a significant role. Some of these problems have been formulated and examined by a number of workers[6-17]. Certain other information concerning technical applications of solid lasers may be found in the monograph of Mikaelyan et al[18].

All the physicochemical processes associated with the study of the structure of complex multicomponent systems employed as liquid lasers may be included in the second class of problems which we have arbitrarily called "chemical". These are problems solved by methods of classical physical chemistry: the thermodynamics of the formation of the complexes and also the study of the rates of chemical reactions.

The range of problems associated with the study of the structures of the complexes formed and their spectroscopic properties over a wide range of the electromagnetic vibration spectrum is no less important. Finally, it is also possible to formulate a further series of problems connected with the investigation of the interaction between radiation and matter.

In view of the large number of problems which must be solved in the making of liquid lasers, we shall consider only some of them. For example, the choice of solvents and their chemical purification, the choice of complex-forming ligands and aprotic acids which improve the properties of the laser systems, and the preparation and selection of compounds in the form of which lanthanides may be introduced into the solvent can be classified as chemical problems.

The requirements which must be met by complex liquid laser systems are dictated by their own properties, i.e. a sufficiently high concentration of active molecules, optical homogeneity of the system, and its stability with respect to light are required. These "physical" requirements themselves have a profound physicochemical basis and need the most far reaching and thorough physicochemical study.

For example, the problem of solubility is one of the most complex. The point is that in multicomponent systems in which the number of components is greater than 4-5 the introduction of each new component improving the optical properties of the system is extremely difficult. This applies in particular to inorganic systems which at this stage appear to be more promising for the formation of liquid lasers.

For example, the inorganic systems include those containing various oxide halides and a wide variety of aprotic acids. The absence of a single quantitative theory of solubility precludes a reliable theoretical prediction of the solubilities of specific lanthanide compounds in various solvents. In the preparation of liquid lasers with fairly high lanthanide concentrations, experimental

data must be employed in each individual case. Very rigorous requirements must be met by the optical homogeneity and transparency of the laser systems, particularly at the emission wavelength, which in turn entails a need for very careful purification of the components.

However, even the most thorough initial purification of the compounds used to prepare the laser liquids does not always yield satisfactory results, since the occurrence of reactions and the formation of side products are possible in the course of the preparation. The side products greatly influence the optical properties of the laser liquid prepared. Therefore the multicomponent liquid systems obtained must be often additionally purified without impairing the laser properties of the system.

The stability of lasers to the action of light also constitutes a very important problem, which concerns the interaction between radiation and matter, involving the stability of solvates and complex species.

The principal components of liquid laser systems are lanthanides, complex-forming ligands, and solvents. We shall attempt to estimate the effect of the system components on the properties of liquid lasers.

II. PRINCIPAL LANTHANIDE ELEMENTS ON WHICH LIQUID LASERS ARE BASED

So far a laser effect in solutions has been obtained for four lanthanides: europium, neodymium, terbium, and gadolinium. The laser systems based on these lanthanides must be immediately subdivided according to the type of "operation" of the lasers. Whereas the systems based on europium, gadolinium, and terbium operate according to the so called "six level" mechanism with transfer of absorbed pumping energy from the ligand to the lanthanide ion, the system based on neodymium gives rise to a laser effect based on a four-level mechanism. In this connection the role played by each component of the laser system as well as the requirements which must be met by the system components will be different.

III. THE NATURE OF THE EQUILIBRIA IN LASER SYSTEMS

In order to prepare new liquid laser systems, detailed studies of their thermodynamic properties are required—these include the types of equilibria occurring in the solutions and the changes in the equilibria when the temperature is altered during the pumping process. The temperature range can be varied within wide limits. We may note that the equilibria arising in such systems can be divided into three types:

1. Solvation equilibria which characterise the interaction of neodymium, europium, gadolinium, and terbium with solvent molecules.
2. Equilibria involved in the formation of complexes by lanthanide ions with various organic and inorganic ligands present in the laser systems.
3. Processes where both types of equilibria can be involved in complex formation.

Lanthanide ions interact in solution with both solvent molecules and with the ligands. In these processes, involving competition between solvation and complex formation, the chemical processes can follow largely one of three pathways, depending on the stability of the complexes formed.

In the formation of a laser system an attempt should be made to ensure that the solvent molecules are displaced from the inner sphere of the complex, since the solvent molecules usually include CH_2 and OH groups, which have a high vibration frequency promoting the leakage of energy in radiationless transitions. A complex of this kind should have a stable inner sphere and the solvent molecules should be in the outer sphere.

The distribution of ligands in the inner sphere obeys the coordination laws but the distribution of molecules in the outer sphere may not in fact be subject to these laws and may be determined statistically. The most complete information about the stability of the solvate complexes of lanthanides formed in different solvents may be provided by the thermodynamic functions for the solvation processes, but few data are available for such functions in non-aqueous solvents[19,20].

Another no less important aspect of the study of laser effects is the coordination number of the lanthanides and the structure and symmetry type of the complexes formed. At the present time much attention is being devoted to them[21].

IV. THE COORDINATION NUMBER OF LANTHANIDES AND THE SYMMETRY TYPE OF SOME OF THEIR COMPLEXES

In the study of the competitive complex formation account must be taken of the variable coordination numbers of lanthanides. In certain early investigations, a coordination number of six was attributed to lanthanides[22-24]. Later studies showed that the coordination number of lanthanides is variable. At the beginning of the lanthanide series the coordination number is 9, but, starting with erbium, it decreases to six[26,27]. Table 1 gives a compilation of studies in which various investigators demonstrated particular coordination numbers of lanthanides using different methods. It is noteworthy that the coordination numbers attributed to a particular lanthanide in solutions should strictly speaking be determined in these solutions. However, many investigators refer to the coordination number determined by the X-ray diffraction analysis of solid lanthanide[26,27]. Such assignment of the lanthanide coordination number to solutions is risky and invalid although in some cases the method is justified.

The coordination number, symmetry, and point group determined by X-ray structure analysis of the crystals sometimes help in the elucidation of the structure of the solvate–ligand complexes formed in the solutions. Table 1 therefore includes, together with the coordination numbers of lanthanides obtained in solutions, certain incomplete data concerning the determination of the coordination numbers in solid salts. Probably solutions with a high salt concentration, close to saturation, bear a marked analogy to the structure of the crystalline compounds. In dilute strong electrolyte solutions, the coordination number and symmetry type of the solvate complex depends mainly on the structure of the solvent surrounding the metal ion. The ligands in the outer coordination sphere have a weaker effect on the solvate complex. A change of solvent leads to a change in the coordination number and the symmetry of the solvate complex[31,33,38]. With increase of ligand concentration and its incorporation into the inner sphere of the lanthanide ion, the coordination number and the symmetry of the solvate structure also change.

In this respect the work of Lugina and Davidenko[34,35] is most instructive and correct. They compared the absorption spectra of the aqueous solutions and the solid hydrates of lanthanide chlorides, bromides, perchlorates, and bromates in order to obtain data on the structure of the lanthanides (neodymium, erbium, and europium) aquo-ions. In particular, it was shown that, together with the dominant form of the $Nd(H_2O)_9^{3+}$ aquo-ion with D_{3h} symmetry, aquo-ions having different structures are also present in the solution.

It has been shown[35] that at higher KSCN and LiCl concentrations, reaching respectively 10 and 14 M, structures with a coordination number of 9 and D_{3h} symmetry, structures with a coordination number of 8, and several structures with equivalent and non-equivalent positions of the ligands coexist.

The spectroscopic method proved extremely fruitful for the comparison of the structures of neodymium complexes with β-diketones in crystals and solutions[36].

Table 1. Coordination numbers of lanthanides determined in various systems.

System	Method	Coordination number	Symmetry type and point group	References
$[Ln(H_2O)_9](C_2H_5SO_4)_3$ Ln = La, Ce, Pr, Nd, Sm, Gd, Dy, Y	X-Ray diffraction structure analysis of crystals	9	Trigonal-bipyramidal symmetry of crystal field, C_{3h}	25
$Ln(ClO_4)_3$—H_2O	NMR	Variable, between 9 at the beginning of lanthanide series and 6 at the end, starting with Pr. 9 or 8 for Gd		26, 27
Ln-*N*-hydroxylene-diaminetetra-acetic acid-H_2O	Potentiometric	Assumed to be 8 between La and Ho		28
$Ln(NO_3)_3$—H_2O Ln=Pr, Nd, Sm, Eu, Gd, Er, Yb, Y. Variable $Ln(NO_3)_3$ concn., between 0.140 and 0.325 mole/1000 g	Derivative plots	6 ± 0.6 for all lanthanides		29
Ce^{3+}-diethylenetriamine-penta-acetic acid-H_2O	Potentiometric	Assumed to be 8		30
$PrCl_3$—H_2O $[Pr(H_2O)_9]^{3+}$	Spectrophotometric	9	D_{3h}	31
$PrCl_3$—CH_3OH	»	9	Solution contains two or more solvated species. $PrCl_2.7CH_2OH^+$ species with C_{2v} symmetry predominate	31
$PrCl_3$—C_2H_5OH	»	9	D_{3h}	31
$PrCl_3$—n-C_3H_7OH	»	Apparently 8	Symmetry lower than D_{3h}	31
$[Nd(H_2O)_9](BrO_3)_3$	X-Ray structure analysis of crystals	9	D_{3h}	32
$NdCl_3$—H_2O	Spectrophotometric	8	D_{2h}	33
$NdCl_3$—CH_3OH	Ditto	8	Lower than D_{2h}	33
$NdCl_3$—C_2H_5OH	»	8	Ditto	33
$[Nd(H_2O)_9]X_3$ X=Cl^-, Br^-, Br, O_3^-, ClO_4^- $c \sim 0.1$ M	Spectrographic. Comparison of crystals and solutions	9	D_{3h}; the existence in solutions of aquo-ions with a different structure together with the dominant form is postulated	34
$Nd(ClO_4)_3$-H_2O-LiCl or KSCN c_{LiCl} = 10-14 M c_{KSCN} = 3-10 M	Ditto	9 or 8	D_{3h}; several structures present in solution	35

Table 1 (cont'd.).

System	Method	Coordination number	Symmetry type and point group	References
$Nd(A)_n^*$ and $Nd(B)_n^*$ in CH_3OH; CH_3OH-H_2O	Spectrophotometric. Comparison of crystals in solution	8	$Nd(AA)_3$ and $Nd(BA)_3$ complexes exist in solution with two solvent molecules in inner sphere	36
$EuCl_3$—H_2O	Spectrophotometric and luminescence	7—8	D_{2h}	34, 37, 38
$EuCl_3$—CH_3OH	Ditto	7—8	C_{2v}	38
$EuCl_3$—C_2H_5OH		7—8	C_{2v}	38
$Eu(TTA)_3 \cdot 2TБФ$ *	Extraction	8	—	39
$[Gd(H_2O)_6Cl_2]Cl$	X-Ray diffraction structure analysis of crystals	8	$P2_1/n$	40
$GdCl_3$—H_2O	Spectrophotometric		D_{2h}	33
$GdCl_3$—CH_3OH	Ditto		C_{2h}	33
$GdCl_3$—C_2H_5OH			C_{2h}	33
$[Gd(H_2O)_9](ClO_4)_3$	NMR	9	—	41
$[Er(H_2O)_6]Cl_2^+$ $[Er(H_2O)_6]I_2^+$	X-Ray diffraction structure analysis of solutions	6	D_{2h}; octahedral environment comprising six water molecules. Two chloride ions occupy opposite the corners of octahedron in second layer	42
$ErCl_3$—H_2O	Spectrophotometric		D_{2h}	33
$ErCl_3$—CH_3OH	Ditto		C_{2h}	33
$ErCl_3$—C_2H_5OH			C_{2h}	33

* Note: A = acetylacetone residue; B = benzoylacetone residue; TTA = thenoyltrifluoroacetone residue; TBP = tri-s-butyl phosphate.

Comparison of the reflection spectra of crystalline neodymium acetylacetonates and benzoylacetonates and the absorption spectra of methanol and aqueous methanol solutions of neodymium complexes with acetylacetone and benzoylacetone with different stoichiometric compositions showed that the $Nd(AA)_3$ and $Nd(BA)_3$ complexes exist in solution with two solvent molecules in the inner coordination sphere.

As data accumulate on the crystal structures of the lanthanide complexes with various organic ligands, they may be employed to investigate the structures of the solutions by spectroscopic methods[44-47].

NMR and X-ray diffraction structure analyses of the solutions are also used to establish the structures of the solvate-ligand complexes[37,41-43]. Nowadays X-ray diffraction structure analysis of liquids is being employed with increasing success for the elucidation of the structural characteristics of the immediate environment of cations in aqueous solutions[48,49].

The data in Table 1 permit certain preliminary conclusions. The coordination number of lanthanum, cerium, praseodymium, neodymium, and gadolinium is 9 or 8, while coordination numbers of 8 and 7 are characteristic of europium. Starting with erbium, the coordination number of lanthanides decreases to 6.

The coordination numbers of lanthanides and the symmetry type of their solvate-ligand complexes are influenced primarily both by the structure of the solvent molecules and that of the ligand molecules coordinated in the inner sphere. In the determination of the composition of the inner-sphere lanthanide complexes, one should bear

in mind the variable coordination numbers listed in Table 1. We may note that a study has also been made where a lanthanide coordination number of six was demonstrated by a derivative plot method[29].

V. PRINCIPAL LIQUID LASER SYSTEMS

The principal data on liquid laser systems are compiled in Table 2. Their analysis permits the following conclusions. While the number of lanthanides used in the preparation of liquid lasers is comparatively small, the number of complex-forming ligands employed for this purpose is fairly large.

A considerable proportion of these ligands have similar properties owing to the mechanism of operation of the laser system. Two laser mechanisms may constitute a kind of barrier, which permits the classification and characterisation of the complexes formed in various solvents.

The majority of laser systems are based on complexes with various β-diketones. These systems involve a single common mechanism in which energy is absorbed by the organic components of the molecule with its subsequent transfer to europium or terbium.

The first eight complexes have approximately the same structure in which the central metal atom is surrounded by four ligands occupying eight coordination sites. Thus the inner sphere of such complexes is completely saturated and all the solvent molecules have been displaced to the outer sphere. According to their structure, these are the usual chelate compounds characteristic of β-diketones.

The study of the luminescence spectra of the octacoordinate europium chelates with the general formula $EuL_4.P$ (where P = piperidine and L is one of the following three β-diketones: benzoylacetone, dibenzoylmethane, or benzoyltrifluoroacetone) led to the conclusion that, among the europium chelates, only the octacoordinate chelates exhibit a laser effect[56]. The following mixtures were employed as solvents: (1) the standard alcoholic solvent (SAS)—a 3 : 1 ethanol–methanol mixture; (2) the dimethylformamide solvent—a 4 : 1 mixture of the standard alcoholic solvent and dimethylformamide (DMF); (3) the nitrile solvent—a 1 : 1 : 1 mixture of acetonitrile, propionitrile, and butyronitrile.

It has been established that chelates with D_4, C_4, and D_2 symmetries are the most effective for the preparation of lasers. The chelates investigated are quite stable with respect to high-intensity radiation pulses. Their chemical stability is determined by the ligand, the solvent, and the concentration of the solution. The chemical structure of the coordinated β-diketones also plays a considerable role.

It is extremely instructive that, out of nine halogeno-substituted derivatives of benzoyltrifluoroacetone (*ortho*-, *meta*-, and *para*-fluoro-, -chloro-, and -bromo-derivatives), only the *ortho*-substituted derivatives can give rise to laser effects in the form of the compounds EuL_4. .DMA. The *ortho*-chloro-compound has the lowest pumping threshold[58].

The ninth and tenth complex (Table 2) are distinguished by the fact that the metal atom in them is coordination-unsaturated. One or two free sites, available to the solvent (acetonitrile or dioxan) molecules, remain in the inner sphere. In the eleventh complex, that of neodymium with pentafluoropropionic acid and *o*-phenanthroline, the variable coordination number of neodymium (which is eight or nine) suggests that the solvent molecules (dimethyl sulphoxide) coordinated to the metal are present in the inner sphere.

The twelfth system, based on neodymium oxide dissolved in selenyl chloride with added aprotic acids, differs somewhat in its physicochemical properties from the systems enumerated above. It is one of the first systems consisting entirely of inorganic components and exhibiting enhanced light stability. Its laser properties are comparable to those of the best specimens of solid systems based on $Nd^{3+}:CaWO_4$ crystals and glasses[63,64].

Analysis of the luminescent properties of this system shows that its structure is closer to that of neodymium crystals in calcium tungstate than to the glasses.

We shall now attempt to describe the chemical reactions occurring when Nd_2O_3 and $NdCl_3$ are dissolved in the $SeOCl_2-SnCl_4$ solvent using the results of certain studies on this problem[65-68]. The reactions occurring in the solvent itself can be described by the following stepwise equilibria:

$$SnCl_4 + 2SeOCl_2 = SnCl_6^{2-} + 2SeOCl^+, \quad (1)$$

$$SbCl_5 + SeOCl_2 = SbCl_6^- + SeOCl^+, \quad (2)$$

$$Nd_2O_3 + 6SeOCl^+ = 2Nd^{3+}_{(solvate)} + 3SeOCl_2 + 3SeO_2. \quad (3)$$

The overall reaction involving the dissolution of neodymium oxide in the $SeOCl_2-SnCl_4$ binary solvent, quoted by Brecher and French[69], can be represented as follows:

$$Nd_2O_3 + 3SnCl_4 + 3SeOCl_2 = 2Nd^{3+}_{(solvate)} + 3SnCl_6^{2-} + 3SeO_2. \quad (4)$$

In these equations the $Nd^{3+}_{(solvate)}$ ion is equivalent to the solvated ion with several selenyl chloride molecules, which are coordinated in the inner sphere with formation of $Nd(SeOCl_2)_n^{3+}$; the $SnCl_6^{2-}$ anions or those of other aprotic acids are coordinated in the outer sphere. The independence of the electronic absorption spectra of neodymium in the visible region of the chemical structure of the aprotic acid may be regarded as indirect evidence that the aprotic acids are combined only in the outer sphere of the solvated neodymium ion. The most intense neodymium absorption bands at 0.53, 0.74, 0.80, and 0.86 nm, corresponding to the $^4G_{5/2}$, $^2G_{7/2}$, $^4S_{3/2}$, $^4F_{1/2}$, $^2H_{9/2}$, $^4F_{5/2}$, and $^4F_{3/2}$ transitions, remain unchanged. Consequently in solution the electrically neutral neodymium complex should have the structure $[Nd(SeOCl_2)n]_2(SnCl_6)_3$. A detailed elucidation of the complex formation processes and the structures of the compounds formed in solution requires further investigation.

Selenium dioxide formed on dissolution of neodymium oxide must be carefully filtered off, since its presence can constitute a serious obstacle to the occurrence of a laser effect[65].

It is noteworthy that, when neodymium chloride is dissolved, the solutions do not contain selenium dioxide particles. The solubility of $NdCl_3$ in pure selenium oxide chloride is limited, but in the $SeOCl_2-SnCl_4$ two-component solvent neodymium chloride dissolves fairly readily. In this case too the final compounds in the oxide chloride solution are probably the solvate–ligand neodymium complexes of the type $Nd(SeOCl_2)_x(SnCl_6)_y^{(3-2y)-}$.

Heller[68] employed lanthanide chlorides obtained by vacuum drying in hydrogen chloride vapour. These compounds usually contain 1–2.5% of water. Traces of water have a marked effect on the luminescence lifetime of the inorganic system, reducing it to 20–30 μs. It is impossible to achieve a laser effect in such systems[65]. Therefore, in order to obtain anhydrous lanthanide chlorides, it is necessary to employ more effective drying conditions[70] or an attempt must be made to separate water and hydrogen chloride vapours during the preparation of the laser system.

Table 2. Properties of the laser solutions.

No.	Complexes	Solvent	Concentration	Laser transition	Laser emission wavelength, Å	Width of laser emission, Å	Life-time, μs	Laser threshold, J	Temp., °K	References
	1	2	3	4	5	6	7	8	9	10
1	EuB_3HB* Thermogravimetric analysis shows that EuB_3 is weakly bound to one molecule of benzoyl acetone	3:1 C_2H_5:CH_3OH (Standard alcoholic solvent)	$2.5\cdot10^{-2}$ *M*	$^5D_0 - {}^7F_2$	6114	—	445 (150° K)		298° K	50, 51, 52
2	$Eu(BTFA)_4P$	CH_3CN Acetonitrile	0.01 *M*	$^5D_0 \rightarrow {}^7F_2$	6119	—	5200	1700	298° K	53
3	$Eu(TTA)_4$.DMA m.p. = 194–195°C	Ditto	$5\cdot10^{-3}$ *M*	$^5D_0 \rightarrow {}^7F_2$	6115	—	—	800	268° K	54, 55
4	$Eu(TFA)_4.HNR_3$ m.p. 194–195°C	»	10^{-2} *M*	$^5D_0 - {}^7F_2$	6119	—	—	800	268° K	54, 55
5	$Eu(BTFA)_4$.I m.p. 194–195°C	»	$7.5\cdot10^{-3}$ *M*	$^5D_0 - {}^7F_2$	6118	—	—	800	268° K	54, 55
6	$Eu(BFTA)_4$.Pyrr m.p.212–213°C	»	Variable, 10^{-2}–10^{-3} M, minimum concn for laser effect 1.5×10^{-3} M	$^5D_0 - {}^7F_2$	6118	40	—	Depends on concn. of complex (850–500)	233÷303°K	54, 55, 56
7	$Eu(O\text{-}Cl\text{-}BTFA_4)$.DMA m.p. 194–195°C	»	$7.5\cdot10^{-3}$ *M*	$^5D_0 - {}^7F_2$	6117.5±1	25	670±20	140–150	294	57, 58
8	$Eu(B)_4Na$	2:5.6:0.8 dimethyl formamide–ethanol–propanol	10^{-2} *M*	$^5D_0 - {}^7F_2$	6111	19 cm^{-1}	—	—	293	59
9	$Tb(TFA)_3$ m.p. 135–137°C	Acetonitrile or 1,4-dioxan	$2.5\cdot10^{-3}$ *M*	$D_4 - {}^7F_5$	5470	—	200	1700	298° K	60
10	$Gd(TTA)_3.B$	Acetonitrile	$2.5\cdot10^{-3}$ *M*	Unresolved		—	—	—	Room	61
11	$Nd(PFA).C_{12}H_8N_2$	Dimethyl sulphoxide	0.2 *M*	$^4F_{3/2} - {}^4I_{11/2}$	10 570	—	50	314–315	298° K	63–68
12	Nd_2O_3—$SeOCl_2$—$SnCl_4$ $NdCl_3$—$SeOCl_2$—$SnCl_4$ Nd_2O_3—$SeOCl_2$—$SbCl_5$ $NdCl_3$—$SeOCl_2$—$SbCl_5$	$SeOCl_2$	0.02–0.75 *N* Nd^{3+}, optimum concn. 0.5 *N*, 500 g litre^{-1} $SnCl_4$	$^4F_{3/2} - {}^4I_{11/2}$	10 566	160	110÷260	6÷40	298° K	62
13	Nd_2O_3—$POCl_3$—$SnCl_4$ $POCl_3 : SnCl_4 = 5:1$	$POCl_3$	Threshold concn. of Nd 3.2×10^{-4} M	$^4F_{3/2} - {}^4I_{11/2}$	10 530	28	170÷200	3300	Room	73, 74
14	$Nd(ClO_4)_3$—$POCl_3$—$TiCl_4$	ditto	0.1 *M*	$^4F_{3/2} - {}^4I_{11/2}$	10 530	4	—	30	ditto	75
15	Nd^{3+}—$POCl_3$—$SnCl_4$ Nd^{3+}—$POCl_3$—$TiCl_4$	»	3%	$^4F_{3/2} - {}^4I_{11/2}$	10 522 10 540	4	120–180 140	28 32	300° K	76
16	Nd_2O_3–$POCl_3\cdot SnCl_4$ $\theta = 4,41\cdot10^{-3}$ *рад*	»	0.1–0.2 *M*	$^4F_{3/2} - {}^4I_{11/2}$	10 600		240	375	Room	77–79
17	Nd^{3+}—$POCl_3$—$SnCl_4$	»	C_{Nd} = 2–10%	$^4F_{3/2} - {}^4I_{11/2}$	10 525±5	10 in planar resonator	260–280			80–82
18	Nd^{3+}—$POCl_3$—$TiCl_4$	»	ditto	$^4F_{3/2} - {}^4I_{11/2}$	10 525±5		210–230			80–82
19	Nd^{3+}—$POCl_3$—$TaCl_5$	»	»	$^4F_{3/2} - {}^4I_{11/2}$	10 525±5	Fabry–Perot	150–180			80–82
20	Nd^{3+}—$POCl_3$—$HfCl_4$	»	»	$^4F_{3/2} - {}^4I_{11/2}$	10 525±5	3 in spherical resonator	150–180			80–82

Note. B = benzoylacetone (HB) residue; BTFA = benzoyltrifluoroacetone residue; P = piperidine; TTA = thenoyltrifluoroacetone residue; DMA = dimethylamine; TFA = trifluoroacetylacetone residue; I = imidazole; Pyrr = pyrrolidine; PFA = pentafluoropropionic acid; B = bipyridyl.

The principal equations of the preparative method for the making of laser solutions were described by Heller[67]. Usually the mixture obtained is coloured brown owing to the the presence of selenium monochloride (Se_2Cl_2):

$$2SeOCl_2 = SeO_2 + SeCl_4, \quad (5)$$

$$2SeCl_4 = Se_2Cl_2 + 3Cl_2, \quad (6)$$

$$Se_2Cl_2 = 2Se + Cl_2. \quad (7)$$

The presence of selenium monochloride may be avoided by oxidation with $KClO_3$.

The chlorine and chlorine dioxide vapours are removed by vacuum treatment. The role of $SbCl_5$ as an aprotic acid improving the solubility of neodymium oxide is analogous to that of $SnCl_4$.

Information about the laser effect of neodymium in a binary phosphorus oxide chloride–aprotic acid system was published almost simultaneously in several papers[72-80]. The principal data for these systems are presented in the Tables and are numbered 12–20. We may note that $BeCl_2$, $ZnBr_2$, $CdCl_2$, $HgCl_2$, BCl_3, BBr_3, $AlBr_3$, $AlCl_3$, $GaCl_3$, $GaBr_3$, $LnCl_3$, $SnBr_4$, $TiBr_4$, $ZrCl_4$, $ZrBr_4$, $AsCl_3$, $NbCl_5$, and $SbCl_5$ as well as the solvents $SOCl_2$ and CCl_4 have also been used in these systems.

Systematic studies by a group of investigators[80-83] suggest that liquid lasers based on phosphorus oxide chloride are more effective than systems based on selenium chloride. There exists also another view, namely that the systems are equivalent in their effectiveness[69].

The dissolution of neodymium oxides and chlorides in a phosphorus oxide chloride–aprotic acid binary solvent resembles in some of its features the dissolution in $SeOCl_2$. The chemical reaction between the binary solvent and neodymium oxide can be represented schematically as follows[69,84,85].

$$Nd_2O_3+3SnCl_4+6POCl_3 = 2Na^{3+}Nd^{3+}_{(solvate)}+3SnCl_6^{2-}+3P_2O_3Cl_4\,. \qquad (8)$$

Here $Nd_{(solvate)}$ is the solvated neodymium ion surrounded by several $POCl_3$ molecules. The study of the structure of this solvate complex and also of its thermodynamic equilibrium with the surrounding medium is of direct theoretical and practical interest for the improvement of the properties of liquid luminescent systems.

Various neodymium compounds have been employed[84,85] to prepare liquid luminescent systems. Most reproducible results were obtained for the $Nd_2O_3-SnCl_4-POCl_3$ system.

The absorption and luminescence spectra of neodymium led to the conclusion that the similarity of the spectra of solutions obtained under different conditions is due to the presence of the same type of immediate environment of the activator in the solution. In the neodymium solvate complex the first coordination sphere consists of $POCl_3$ molecules coordinated to neodymium via oxygen[86]. It is sufficiently stable to form identical luminescence centres in several versions of the solution which the present author investigated, this being reflected in a similarity of the spectra. The existence of a fairly stable solvate shell has been confirmed by Antipenko et al.[85], who showed the occurrence of energy transfer between lanthanide ions in the $POCl_3-SnCl_4$ system.

Different workers suggest a wide variety of metal halides as aprotic acids[63-83]. Aprotic acids play an important role in the enhancement of the effectiveness of luminescence [quantum yield of luminescence (Ed. of Translation)]. This does not involve merely an improvement of the solubility of neodymium salts; for example, when neodymium perchlorate was employed[75], the metal concentration in solution was fairly high, since the perchlorate is readily soluble in $POCl_3$, but the luminescence intensity of the $POCl_3-Nd(ClO_4)_3$ solution was low. The luminescence of the same solutions increases abruptly by a factor of five when small amounts of aprotic acids are added.

The present author explains the increase of the effectiveness of the luminescence by the association of chloride anions with the aprotic acid. The most effective aprotic acids are $SnCl_4$, $SbCl_5$, $TiCl_4$, $TaCl_5$, and $HfCl_4$. The behaviour of these compounds in $POCl_3$ has already been partially investigated; thus the following equilibrium (equilibrium constant K) has been suggested for the reaction of $SbCl_5$ and $POCl_3$:[87]

$$Cl_5SbOPCl_3 \rightleftharpoons SbCl_6^- + POCl_2^+\,, \qquad (9)$$

where $K = 4\times10^{-6}$. For the next reaction stage,

$$SbCl_6^- + POCl_3 \rightleftharpoons Cl_5SbOPCl_3 + Cl^-; \qquad (10)$$

K not exceeding 10^{-9}. The mobilities obtained from conductimetric data are more characteristic of non-solvated ions.

VI. SOLVENTS

The principal physicochemical information about the nature of the solvents is presented in Table 3. The number of solvents in which laser effects of lanthanide ions have been observed is small.

All the solvents can be arbitrarily divided into two groups. Proton-containing organic compounds may be included in the first group and aprotic solvents in the second. On introduction of binary solvents such as metal oxide halide–aprotic acid, the number of solvents which can be used to obtain laser systems will increase.

It is noteworthy that three-component solvents of the type $POCl_3-SOCl_2$–aprotic acid have already appeared[81]. The addition of $SOCl_2$, carbon tetrachloride, and certain other components tends to extend the region of the liquid state and to stabilise neodymium solutions while the luminescent and laser characteristics are retained[81].

Thus multicomponent liquid laser systems, the individual components of which will successfully supplement one another in creating the optimum operating characteristics of the system, will probably be employed in the future. The use of a number of components in the test system is reasonable, since none of the solvents usually has the entire set of the necessary properties. All this applies equally to proton-containing organic solvents and to aprotic solvents[89,90].

An attempt has been made[90] to assess the prospects for the application of various solvents in liquid laser systems. Hydrogen-bonded organic solvents have been mainly examined. Analysis of the physicochemical properties of solvents makes it possible to find ways for the selection of the most effective solvents in broad outline only.

VII. THE STRUCTURE OF THE COMPLEXES AND ITS RELATION TO LUMINESCENCE

An excited lanthanide ion, for example a neodymium ion, can lose its energy via two main mechanisms. One may assume that the first mechanism whereby the energy of the excited neodymium ion is dissipated is a direct transfer to the surrounding medium via vibrations. The mechanism of this type of transfer has been studied by different investigators on various models[63,91,92].

In the second case account must be taken of the high neodymium concentration as a result of which self-quenching of neodymium occurs[93] owing to an energy jump between adjacent neodymium atoms[94]. It is suggested that the radiationless energy transfer from neodymium and other lanthanides is analogous to the processes occurring in organic compounds[95-97] and also in inorganic ions[98-102].

Table 3. Solvents.

Name and structural formula	M	Dielectric constant ε	M.p.-b.p., °C	n_D	d, g cm^{-3}	κ, Ω^{-1} cm^{-1}	η, cP	References
CH_3OH	32.04	32.63	−97.47÷64.56	1.3286 at 15°	0.78675	$1.5\cdot10^{-9}$	0.5445	88
C_2H_5OH	46.086	24.3	−117.3÷78.327	1.3594	0.78506	$1.35\cdot10^{-9}$	1.078	88
Standard alcoholic solvent, 3:1 C_2H_5OH-CH_3OH								
Acetonitrile CH_3CN	41.052	37.5 at 20°	−45.72÷81.60	1.34163	0.77683	10^{-8}	0.3448 at 30°	89
Dioxan $C_4H_8O_2$	88.1	2.209	11.7÷108.8	1.42436	1.03375 at 20°	$5\cdot10^{-15}$	1.439	89
Dimethylformamide	73.01	36.71	−61÷153.0	1.4294	0.9443 at 25°	$2\cdot10^{-7}$	0.796	89
Propyl alcohol solvent−2:5.6:0.8 dimethylformamide-ethyl alcohol-propyl alcohol	60.09	19.7 at 25°	−127÷97.2	1.3873	0.80753 at 15°	$5\cdot10^{-8}$	2.18 at 20°	88
Dimethyl sulphoxide $(CH_3)_2SO$	78.13	48.9	18.2÷189		1.100	$3\cdot10^{-3}$	2.473 at 20°	89
Selenyl chloride	165.9	46.2 at 20°	8.5÷168	2.64 at 25°	2.44 at 25°	$2.5\cdot10^{-5}$		87, 88
Phosphorus oxide chloride $POCl_3$	153.33	13.9	1.25÷105.8	1.460	1.648	$2\cdot10^{-8}$	1.018	87

The main conclusions which may be drawn from these studies reduce to the condition that the solution should not contain light atoms with a high bond vibrational energy for example hydrogen atoms or at any rate these atoms should not be linked directly by chemical bonds to atoms coordinated to the lanthanides.

The studies of Heller and Lempicki confirm these postulates in broad outline.

Earlier experiments in organic solutions showed that the removal of quenching elements from the intervening spaces between excited ions and vibrating adjacent molecules rapidly increases the luminescence quantum yield[103]. An aqueous neodymium chloride solution may be adopted as a standard solution with the specified minimum quantum yield. The replacement of an aqueous solution by a deuterated solution increases the luminescence factor fivefold. The replacement of water by a solvent such as dimethyl sulphoxide, in which the solvating oxygen atoms are not linked to hydrogen atoms, increases the luminescence intensity by a factor of 10 and the quantum yield rises almost by two powers of 10 compared with aqueous solutions; on the other hand, deuteration increases further the luminescence yield by a factor of three. From this standpoint, organic halogeno-derivatives are the most suitable compounds, since they do not contain atoms lighter than carbon.

Therefore it is also not surprising that the most effective luminescent systems proved to be those in inorganic solvents, of the type $Nd^{3+}-SeOCl_2$−aprotic acid or $Nd^{3+}-POCl_3$−aprotic acid; the quantum yield for the first system is sometimes higher than the luminescence yield in aqueous solutions.

Table 4 presents the principal characteristic vibration frequencies of groups of atoms in the solvent and ligand which in solvation and complex formation processes may be in the immediate vicinity of the central atom with a specified energy store[104-106].

Table 4. Characteristic bond vibration frequencies in various components of laser systems.

Compound	Bond	Absorption region, cm^{-1}	References
Primary alcohols	O−H	3650—3590	104
Primary alcohols	C−H	1050	104
Nitriles	−C≡N	2260—2240	104
Sulphoxides	>S=O	950	106
Selenyl chloride	>Se=O	955	105, 106
Phosphorus oxide chloride	→P=O	486, 1261	106
β-Diketones	−C(=O)−CH$_2$−C(=O)−	1646—1540	104
Primary amines	>N−H	3506—3300	104
Dimethylamines	CH_3>N− CH_3	2825—2810 2775—2765	104
Skeletal vibrations of five-membered heterocycles	Imidazole, pyrrolidine	1598—1510	104
Nitrogen-containing heterocycles	N−H	3440—3400	104
Stretching vibrations of six-membered rings	Piperidine	1640—1555	104
Carboxylic acid salts	O=C−O$^-$	1610—1550	104
Tin tetrachloride	$SnCl_4$	368	106
Antimony pentachloride	$SbCl_5$	356	106
Titanium tetrachloride	$TiCl_4$	388	106
Anion	$SnCl_6^{2-}$	311	106
"	$SbCl_6^-$	337	106
"	$TiCl_6^{2-}$	463	106

The smallest distances between the excited lanthanide levels for Nd^{3+} ($^4F_{3/2}-{}^4I_{15/2}$) Eu^{3+} ($^5D_0 \rightarrow {}^7F_6$), and Tb^{3+} ($^5D_4-{}^5F_5$) are respectively 5500, 12500, and 18300 cm^{-1} [107,108], while the bond vibrational energies in phosphoryl and selenyl groups, tin tetrachloride, and antimony pentafluoride are much lower. The stretching vibrational energies of the O−H and C−H bonds are much closer to the energy differences between the excited levels in lanthanide ions.

The study of lanthanide complexes in aprotic solvents led to the development of new views on their structure and also made it possible to discover a relation between the dissipation of energy from the excited ions to the surrounding medium as a function of the type of bond. These concepts were used initially by a group of investigators for polyphosphoric acids which had been subjected to extensive chlorination and fluorination[86]. Extensive chlorination of polyphosphoric acids leads to the occurrence in solutions of non-bridged structures isolated from the surrounding medium by halogen atoms. Important additional information is provided by studies on the vibrational spectra, which showed that in aprotic solvents lanthanide ions are surrounded by oxygen atoms. These investigations also led to the discovery that unchanged metal halide molecules are absent from the solutions.

The determination of the crystal field parameters and the study of the vibronic spectra made possible a number of conclusions concerning the immediate environment of lanthanide ions in solvents such as H_3PO_4, $SeOCl_2-SnCl_4$, $H_2SeO_3-POCl_3$, and $POCl_3-SnCl_4$. These data show that the ion has C_{4V} symmetry with some distortion. The immediate environment of the ion consists of P—O groups or, less probably, [109].

In conclusion one must emphasise that the discovery of liquid luminescent and laser systems based on inorganic solvents with heavy atoms gives rise to the hope for a rapid development and application of these systems as lasers, which will not be inferior in their properties to solid lasers. One should also bear in mind liquid laser systems based on organic solutions of lanthanide chelates. The studies in this field are still far from completion.

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The Chemistry of New Atoms†

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The physicochemical interaction of hydrogen-like positronium and muonium atomic systems, in which the proton is replaced by a positron or a μ^+-meson, and mesonic atoms containing a μ^-- or a π^--meson instead of an electron have been examined. The nuclear-physical methods for the investigation of processes involving the new atoms have yielded information which significantly supplements that available from the usual research techniques.
The bibliography includes 123 references.

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I. INTRODUCTION

The last two decades have been distinguished by the appearance and development of a new research field intermediate between the physics of elementary particles and chemistry. It concerns the chemistry of "new atoms" in which either an electron or a proton is replaced by another negatively or positively charged elementary particle.

Atoms in which there is a negative meson instead of one of the electrons are called mesonic atoms. On forming a chemical bond with other "ordinary" atoms, mesonic atoms can form also the so called mesonic molecules.

The most thoroughly investigated examples of new atoms of this type are the μ- and π-mesonic atoms. They will be the only ones considered in the appropriate sections of the present review.

However, in principle, there is also a possibility of the existence of K-mesonic atoms and new atoms in which instead of an electron there is a negative hyperon, an antiproton, or an antihyperon.

The radius of the nth Bohr orbital is $a_n = \hbar^2 n^2/\mu Z e^2$, in which $\mu = Am_N m/(m + Am_N)$ is the reduced mass, m the mass of the particle in the orbital, m_N the mass of the nucleon, A the mass number of the nucleus, and Z its charge.

Therefore the radii of the first Bohr orbitals of the hydrogen-like μ- and π-mesonic atoms are respectively about $2.5 \times 10^{-11}/Z$ cm and $1.9 \times 10^{-11}/Z$ cm, which are closer to nuclear rather than atomic dimensions. This is

† In the compilation of this review data known to the authors by 1st March 1970 were employed.

even more true of the K-meson, antiproton, and hyperon atoms (for example $a_1 \simeq 5 \times 10^{-13}$ cm for K-mesonic sodium and $a_1 \simeq 2.7 \times 10^{-13}$ cm for antiproton-sodium). As a result, the effective charge of the nucleus of the mesonic atom or an even heavier new atom of this type is z only for large values of n, of the order of $n \simeq \sqrt{m/m_0}$ (m_0 is the mass of the electron), and decreases by unity when the particle replacing the electron passes to the first orbitals.

Atoms in which the proton is replaced by another positive particle are named after the particle with the ending "onium". The penetration of any positive particle into the nucleus is hindered by electrostatic repulsion which can be counteracted only by attraction due to nuclear forces. Therefore, for the lightest positive particles (leptons), i.e. the positron and μ^+-meson, which do not enter into nuclear interactions, atoms of the "onium" type are possible only without a nucleonic nucleus, the positive leptons replacing the sole nucleon (the proton). An atom comprising a positron and an electron is called positronium (Ps) and an atom comprising a μ^+-meson and an electron is called muonium (Mu). Both positronium and muonium may be regarded as light hydrogen isotopes, positronium being the lightest of all the new atoms—it is at the same time the only atom altogether without a nucleus. Indeed, since both constituent particles of positronium have equal masses, the centre of gravity about which they both rotate does not approach either of them (such a particle would have played the role of a nucleus) but is located exactly in the centre.

A nuclear proton can be replaced also by a positively charged hyperon just as a neutron can be replaced by neutral hyperon. This gives rise to the so called hypernuclei and the corresponding hyperatoms. However, the structure of the electron shells of hyperatoms and their chemical properties hardly differ from those of the atoms with the same nuclear charge and therefore hyperatoms are not usually included among the "new atoms".

All the new atoms are unstable. The upper limits to the lifetimes of atoms with charged μ- or π-mesons are the intrinsic lifetimes of these particles in a vacuum ($\tau_\mu \simeq 2.2 \times 10^{-6}$ s, $\tau_\pi \simeq 2.5 \times 10^{-8}$ s) in relation to the decomposition processes $\mu^\pm \rightarrow e^\pm + \nu(\tilde{\nu}) + \tilde{\nu}_\mu/(\nu_\mu)$ and $\pi^\pm \rightarrow \mu^\pm + \nu_\mu(\tilde{\nu}_\mu)$ (ν is a neutrino and $\tilde{\nu}$ an antineutrino).

Each of the constituent particles of positronium is itself stable but, being a particle and an antiparticle, the electron and positron annihilate one another with emission of gamma-quanta, which is the reason for the instability of positronium and its very short lifetime (10^{-7}–10^{-10} s in a vacuum).

From the chemist's point of view, the main interest of the study of new atoms consists in the fact that chemical and crystalline environments influence their lifetimes and various characteristics of their destruction.

The first stage of studies in the chemistry of new atoms is the elucidation of the laws governing such influence and the verification of how specified changes in the chemical or crystal structure of the substance or the changes established in independent experiments influence the fate of new atoms.

The second stage of such investigations of the greatest importance to chemistry, in which chemistry assumes the role of a "consumer", is the determination of new structural-chemical data on the kinetics and mechanism of chemical processes based on the observation of particular characteristics in the formation, transformation, and destruction of new atoms.

At present, the mesochemical studies on μ- and π-mesonic atoms and muonium are still in the first stage, while the work on the physical chemistry of the positron and positronium have already passed to the second stage and has begun to yield new information of general importance to chemistry.

II. POSITRONIUM

1. General Characteristics of the Annihilation of Positrons and the Physical Properties of Positronium

The annihilation of positrons and the formation and destruction of positronium have been described in monographs[1,2], reports at the 1965 Conference in Detroit (USA),[3] compilation tables[4], many reviews[5–18] and articles containing an extensive bibliography (see, for example, Refs. 19 and 20), and about 400 original papers. The aim of the present review is not to give any sort of complete list of literature on this problem and we shall confine ourselves to the description of the general information of the greatest significance to chemists, concentrating attention on the latest work.

The positron, predicted theoretically by Dirac and discovered in 1932 by Anderson, is the antiparticle of the electron having the same mass ($m_0c^2 = 0.511$ Mev) and the opposite positive electrical charge ($e = 4.8 \times 10^{-10}$ CGSE). The hitherto unknown mutual annihilation process was first observed for the positron (e^+) and the electron (e^-); the process is characteristic of the interaction of particles and antiparticles in general and in the present case is accompanied by the emission of γ-quanta. The annihilation on collision between an electron and a positron can involve the emission of either two or in rare cases (probability 1/373) of three γ-quanta. One-quantum or quantumless annihilation require the participation of a third body and their probabilities are altogether low.

In laboratory experiments positrons are obtained from radioactive isotopes, for example sodium-22 or copper-64, which emit positrons with a maximum energy of several hundred keV. The positrons emitted by the sources initially behave like electrons—they are retarded expending their energy on the ionisation and excitation of the surrounding molecules. Up to energies of several tens of electron-volts, the role of annihilation is negligibly small and almost all the positrons "survive" until the attainment of the above low energies and are only then annihilated. By virtue of the possibility of recording the annihilation quanta, the positron is, as it were, a labelled electron the fate of which, from its appearance in the substance until its destruction by annihilation, can be followed. According to Dirac, the 2γ-annihilation cross-section for the positron and electron moving relative to one another at a velocity $v \ll c$ ($c = 3 \times 10^{10}$ cm s^{-1}) is

$$\sigma_D = \pi r_0^2 \frac{c}{v} = \pi \left(\frac{e^2}{m_0c^2}\right)^2 \cdot \frac{c}{v} \simeq 7.4 \cdot 10^{-15} \cdot \frac{1}{v} \text{ cm}^2 . \qquad (1)$$

There exist three principal variants of the annihilation, each of which can be isolated experimentally and each provides certain specific information about the properties of the medium in which the annihilation takes place.

The first pathway involves the annihilation in free or quasi-free (i.e. without the involvement of the ionic framework) collisions of positrons with electrons. If the two particles were at rest at the instant of mutual annihilation, then the two annihilation quanta would have absolutely identical energies (equal to m_0c_2) and the angle of their divergence would be exactly 180°. The experimentally

observed negligible deviations of the energies (by several electron-volts) and angles (by several milliradians) from the above values permit a direct recording of the count distribution of the conductivity and valence electrons which annihilate the positrons (their penetration to the region of the inner atomic orbitals is prevented by the Coulombic repulsion by the nucleus) and the observation of the anisotropy of such distribution relative to particular specified directions in crystals and molecules and the changes in it during phase transitions.

Another annihilation pathway is via the formation of combined states of the positron with neutral molecules (e^+M) or with anions (e^+A^-). From a theoretical standpoint, the structure and analysis of the wave functions of molecules of the type e^+H^- or, what amounts to the same thing, positronium hydride PsH, are of interest[20]. One cannot rule out the possibility of the formation of a completely new type of chemical bond of the kind He$-e^+-$He. The formation of a virtual or combined level of the e^+M system (as a result of the polarisation by the positron of the electron cloud of the atom or molecule) leads to a characteristic "resonance annihilation" phenomenon the cross-section of which is sometimes tens and hundreds of times greater than the Dirac σ_D. There is also a possibility of the formation of collective (polaron) states of the positron or bonds between the positron and lattice defects in ionic crystals. Of the problems which are not considered in a monograph by one of the present authors[1], we shall mention here only the model of the optical positron[21] and new experimental methods, based on it, for the determination of a parameter of great importance for structural chemistry—the effective charges of the anions (atoms of Group VII and VI elements) from data for the angular correlation between the annihilation quanta[22] and the lifetimes of positrons[23] in ionic media.

We shall also mention recent interesting observations[24] which established a very marked influence of even low concentrations of F-centres in KCl (approximately 3×10^{-4} of the number of regular Cl^- sites) on the type of angular correlation of the annihilation γ-quanta and thereby again demonstrating the high sensitivity of positron methods to any kind of breakdown in the regularity of crystal lattice structures.

The third pathway for the annihilation of positrons—via the formation of positronium atoms—is of greatest interest for a wide range of problems in modern physical chemistry and is in fact considered below.

The possibility of the existence of combined states of the electron–positron system was postulated in 1934,[25] the name "positronium" was proposed for the electron–positron atom in 1945,[26] and the chemical symbol Ps was put forward in 1959.[27] The existence of positronium was demonstrated experimentally by Deutsch in 1951.[28] The mass of positronium is 920 times smaller than the mass of the hydrogen atom but its reduced mass $\mu_{Ps} = m_0/2$ is only twice as small as the reduced mass of the hydrogen atom $\mu_H \simeq m_{i0}$. Accordingly the ionisation potential of positronium in the ground (1s) state $V = e^4\mu z^2/2\hbar^2 n^2$ ($\mu = m_{i0}/2$, $z = 1$, and $n = 1$) is twice as small as the value for hydrogen and amounts to $V_{Ps} \simeq 6.77$ eV. The distance between the positive and negative charges, which in the case of hydrogen is defined as the radius of the first Bohr orbital, is twice as large in positronium and is close to 1.06 Å (when $n = 1$). In the present case this distance is, however, not the radius but the diameter of the atom.

There exist two ground states (1S; $n = 1$) of positronium—the triplet state $^TPs(^3S_1)$ or orthopositronium o-Ps with parallel spins of e^- and e^+ and the singlet state $^SPs(^1S_0)$ or parapositronium p-Ps with antiparallel spins of e^- and e^+. The total moment of o-Ps is $J_T = 1$ and in this case three substates are possible, differing in the magnetic quantum numbers: $m = +1$, 0, or -1. For p-Ps, $J_S = 0$ and $m = 0$. Correspondingly, the statistical weight $2J_T + 1$ of o-Ps is three times larger than for p-Ps and in the formation of positronium o-Ps arises in 75% of cases and p-Ps in only 25% of cases.

In accordance with various selection rules, p-Ps is annihilated with the emission of two γ-quanta and o-Ps with the emission of three γ-quanta. As a result, the intrinsic lifetime of singlet positronium is much shorter than that of triplet positronium. The lifetime of p-Ps in a vacuum is

$$\tau_S^0 = 2\frac{\hbar^2}{m_0e^2}\cdot\frac{1}{cr_0^2} = 1.25\cdot 10^{-10}\text{s}. \qquad (2)$$

while that of o-Ps is higher by a factor $9\pi/4(\pi^2 - 9)(\hbar c/e^2) = 1115$ and amounts to $\tau_T^0 = 1.4 \times 10^{-7}$ s.

As a result of the hyperfine splitting of the 1S state of positronium, the energy of o-Ps exceeds that of p-Ps by an amount

$$\Delta W = {}^TW - {}^SW = \frac{7}{12}\left(\frac{e^2}{\hbar c}\right)^4 m_0c^2 = 8.4\cdot 10^{-4}\text{ eV} \qquad (3)$$

(to within the so called radiation corrections).

In fairly strong external magnetic fields, a "good" quantum number is no longer the total moment of positronium J but m, the states with $m = 0$ and $J = 1$ and with $m = 0$ and $J = 0$ are mixed, and the contribution by the 2γ-annihilation of positronium increases (in a vacuum) from 25 to 50%. External fields alter the energies of the sublevels with $m = 0$, increasing the energy for the state with $m = 0$ and $J = 1$ and correspondingly decreasing it for the state with $m = 0$ and $J = 0$ by $\Delta W(1 + x^2)^{1/2}/2$, where $x = (2e\hbar/m_0c)(H/\Delta W) = 2.75 \times 10^{-2} H$ (kilogauss), but do not affect the energies of the $m = \pm 1$ states. An additional decrease of the probability of the 3γ-annihilation of triplet positronium can arise due to the magnetic dipole transitions ($m = \pm 1$) $\rightarrow$ ($m = 0$) in a high-frequency electromagnetic field at the resonance frequency

$$\nu = \frac{\Delta W}{2\hbar}[\sqrt{1 + x^2} - 1].$$

For fields of about 10 kG, the frequency $\nu \simeq 3000$ MHz, so that the experiments on the quenching of the 3γ-annihilation of positronium by a high frequency field, which were carried out for the first time by Deutsch[29] and made it possible to determine with high accuracy ΔW, were the first experiments on the microwave spectroscopy of positronium.

2. General Chemical Properties of Positronium. The Quenching of Positronium. Principal Differences between Positronium and Hydrogen

Positronium, which is the lightest hydrogen-like atom and constitutes a model free radical, is also a kind of labelled atom, the properties, the lifetime, and the mechanism of the destruction of which greatly depend on the properties of the surrounding medium. The short intrinsic lifetime of orthopositronium makes it possible to use this time as a convenient standard in the investigation of rapid reactions involving atoms of the hydrogen type and to observe and study the role of diffusion and quantum (tunnel effect) factors in the kinetics of such reactions.

As a rule the duration of chemical reactions in which positronium is involved lies within the limits between the characteristic lifetimes of the long-lived form (ortho-positronium, 10^{-9} s in the condensed phase, 10^{-7}–10^{-8} s in gases, $\tau_T^0 = 1.4 \times 10^{-7}$ s in a vacuum) and of the short-lived form (parapositronium, $\tau_S^0 = 1.25 \times 10^{-10}$ s). Therefore a decrease of the lifetime (the quenching of positronium) constitutes in the first place the quenching of orthopositronium, the replacement of the annihilation of the positron in the ^{T}Ps state by other types of annihilation.

The processes involving positronium which lead to the quenching of ^{T}Ps include the following: (1) annihilation by "foreign" electrons at the instant of collision between Ps and other atoms or molecules—the so called "pick-off" annihilation; (2) ortho-para conversion in the interaction with paramagnetic species, for example $^T\mathrm{Ps}(\uparrow\downarrow) + \dot{\mathrm{N}}\mathrm{O}(\downarrow) \rightarrow {}^S\mathrm{Ps}(\uparrow\downarrow) + \dot{\mathrm{N}}\mathrm{O}(\uparrow)$; (3) substitution reactions, for example, $\mathrm{Ps} + \mathrm{Cl}_2 \rightarrow \mathrm{PsCl} + \mathrm{Cl}$; (4) addition reactions, for example, $\mathrm{Ps} + (\mathrm{CF}_3)_2\dot{\mathrm{N}}\mathrm{O} \rightarrow (\mathrm{CF}_3)_2\mathrm{NOPs}$, as a result of which the positron is brought into the field of many electrons, as in pick-off annihilation; (5) oxidation reactions, for example, $^T\mathrm{Ps} + \mathrm{Fe}^{3+} \rightarrow e^+ + \mathrm{Fe}^{2+}$, which lead to the formation of a rapidly destroyed free positron.

In substitution, addition, and oxidation reactions, positronium behaves as a chemical analogue of hydrogen. However, because of the very great difference between the masses of hydrogen and positronium, there are many differences in the structure of their compounds, the energies of their formation, and the kinetics of their chemical reactions.

While an HA molecule (A is any atom) should be regarded as a two-centre molecule, its analogue PsA = e^+A^- is better characterised as a one-centre molecule, namely as an A atom with mixed electron and positron clouds. This is markedly reflected in the bond energy—for example, while the A_2 bond energy is close to 4.5 eV, the energy for HPs is estimated as 0.657 eV [20] and for Ps_2 as 0.11 eV.[30] The stability of any PsA molecule must be lower than that of HA if only because, with increase of the reduced mass μ of the molecule, the energy of the zero-point vibrations, from which the dissociation energy is reckoned, must increase. In principle $\hbar\omega_0 \propto 1/\sqrt{\mu}$, but in fact that ratio $(\hbar\omega_0)_{PsA}/(\hbar\omega_0)_{HA}$ probably never reaches the value

$$\sqrt{\frac{\mu_{PsA}}{\mu_{HA}}} \simeq \sqrt{\frac{m_H}{m_{Ps}}} \simeq 30 .$$

Nevertheless any reaction involving the substitution of H by Ps, $HA + Ps \rightarrow PsA + H$, is probably endothermic.

As stated above, the ionisation potential of the H atom is twice as high as for Ps. Therefore in the gas phase the oxidation of positronium by hydrogen is a highly exothermic process: $H^+ + Ps \rightarrow H + e^+ + 6.8$ eV. Since however the heat of hydration (and in general the heat of solvation) of the proton, which is close to 11 eV, is much higher than for the positron (one can assume arbitrarily that this heat is 1.5–2 eV, as for the electron), the oxidation of positronium by hydrogen in aqueous solution is endothermic and hardly occurs to an appreciable extent: $H^+_{aq} + Ps_{aq} \rightarrow H_{aq} + e^+_{aq}$ (~ 2.5 eV). The electron affinity of the hydrogen atom (0.75 eV) also exceeds the analogous quantity for positronium (estimated [31,32] as ~ 0.20 eV).

In comparing the rates of reaction of hydrogen and positronium, one should bear in mind not only the difference between the heats (the heat of an endothermic reaction is equal to its minimum possible activation energy), the pre-exponential factors (the thermal velocity of Ps atoms is about 30 times higher than that of H), and the diffusion coefficients, which reach $D \simeq 3 \times 10^{-4}$ cm^2 s^{-1} for Ps in various solvents (Becquerel [1], Chapter VII), but also the possibility of tunnel transitions within a particle as light as positronium under conditions where such transitions are virtually ruled out for H atoms. We obtained in our investigations [33,34] the temperature T_{tun} below which tunnel transitions predominate exponentially over the Arrhenius (over-the-barrier) transitions: $T_{tun} = (\hbar/k\pi d)\sqrt{E/\mu}$, where k is the Boltzmann constant, μ the reduced mass of the tunnelling system, d the width of the potential barrier, and E its height. For free positronium, the temperature T_{tun} is approximately 30 times higher than for H atoms and sometimes amounts to hundreds of degrees. Therefore in gas-phase reactions of positronium, a non-activation tunnel mechanism is extremely likely.

The appearance of a tunnel effect is not the sole expression of the wave properties of positronium associated with its low mass and consequently with its high De Broglie wavelength. For a thermal positronium atom at room temperature, $\lambda\!\!\!^{-} \simeq 9$ Å, so that the cross-sections for processes involving positronium can reach in principle $4\pi\lambda\!\!\!^{-2} \simeq 10^{-13}$ cm^2.

Yet another kinetic difference between the reactions of hydrogen and positronium, due to the unusually low mass of the latter, consists in the fact that the electron transitions between positronium and another atom cannot be regarded as adiabatic, without a change in the distance between the positron and the nucleus of the other atom.

Finally the low mass of positronium leads to an unusual form of the excitation functions for its endothermic substitution reactions ($Ps + AB \rightarrow APs + B$), which differ appreciably from those for H atoms, but are close to the excitation functions for dissociative electron capture ($\bar{e} + AB \rightarrow A\bar{e} + B$). The cross-sections for the above reactions of Ps and an electron have a sharp maximum directly at the threshold and the maximum cross-section is very sensitive to the threshold energy and provides a method for its determination. When the energy increases above the threshold value by an AB vibration quantum, the substitution cross-section decreases sharply [35].

The above factors make it difficult to transfer directly the results of positron studies to reactions of hydrogen atoms, but they give rise to the possibility of many specific applications of the positron method in chemistry, which will be described below.

3. The Probability of the Formation of Positronium and Its Inhibition Processes

One of the principal characteristics of the annihilation of positrons is the probability P of the formation of positronium. The simplest estimate of this quantity is provided by the so called Ore model [36] illustrated in Fig. 1. Here V denotes the ionisation potential of the molecules of the medium and E the excitation energy for their first electronic level. As long as the kinetic energy of positrons exceeds E and particularly V, the energy expenditure on ionisation and excitation predominates. On the other hand, when the energy of positrons is lower than $V - 6.8$ eV, the formation of positronium is simply

impossible on energy grounds. The range of positron energies between E (upper limit) and $V - 6.8$ eV (lower limit), in which the dominant positron interaction process is the formation of Ps, is called the Ore gap. For a rectangular spectrum of retarded positrons, the Ore model gives $6.8/V > P > [E - (V - 6.8)]/E$, which holds fairly well for simple gaseous systems. For example, for argon $V = 15.8$ eV and $E = 11.6$ eV, whence $0.43 > P > 0.22$, while experiment gives $P = 0.30$.

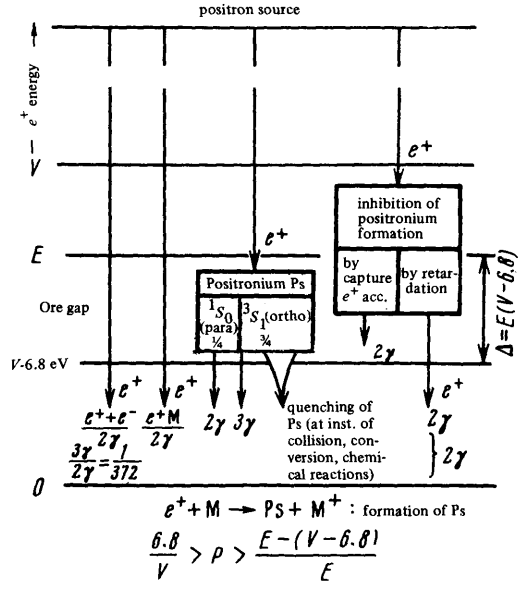


Figure 1. A schematic representation of the processes involving the formation and destruction of positronium, illustrating the Ore model and possible deviations from it.

In the condensed phase predictions based on the Ore model must be appreciably modified if only because account must be taken of the affinity of the medium for electrons, positrons, and positronium atoms. However, even without these complicating factors, the situation may alter (even in gases) in consequence of various inhibition processes, which lower the probability of the formation of positronium (Fig. 1). These are the capture of positrons, competing with the formation of positronium and with the elastic retardation of positrons (resulting in their slow passage through the Ore gap), which altogether removes positrons "from play", and non-elastic retardation of positrons, which rapidly brings them below the Ore split into the region of low energies, where positronium is no longer formed.

Both types of inhibition—by capture (capture inhibitors) and retardation (retardation inhibitors)—may be due to the medium itself in which the annihilation is investigated (auto-inhibition) and to different additives (inhibition by impurities) at varying concentrations.

The foregoing shows that the observation of changes in the probability of the formation of positronium and the study of various processes involving the inhibition of such formation can yield information about the various ways in which positrons are captured (for example, capture from a complex with annihilation: $e^+ + AB \rightarrow ABe^+ \rightarrow 2\gamma$, or capture with dissociation: $e^+ + AB \rightarrow A + Be^+ \rightarrow 2\gamma$), about their non-elastic retardation, and about the excitation of the electronic, vibrational, and rotational levels of the inhibitor molecules. An additional source of information comes from the increase of the probability of the formation of positronium when static external electric fields are applied, because the field accelerating positrons can return to the Ore gap some positrons with an energy less than $V - 6.8$ eV. The combination of such accelerating effects of the field and the loss of positron energy in elastic and non-elastic collisions is comparatively readily susceptible to calculation and can serve as a basis for the estimation of the cross-sections for different types of interaction involving positrons.

Thus different ways become available for obtaining data about the competition between the ionisation of molecules, their electronic excitation, and the capture of electrons by positrons with energies of the order of several electron-volts and about the relative contributions of the cross-sections for the elastic and non-elastic scattering and the capture of positrons.

When applied to the gas phase, the relevant field of study has been called by Massey "positronics" [37] and constitutes a useful addition to gaseous electronics. In the condensed phase positronic research techniques are applicable also under conditions where the corresponding data are altogether lacking even for electrons. In this connection, one of the most interesting problems is, for example, the study of the changes in the nature of the retardation of positrons on passing from a gas to a liquid and further to a solid, as a result of the appearance of collective interactions.

4. Principal Experimental Methods in Positronium Chemistry

According to the foregoing, the main subject of observations in experiments with positronium is two characteristics of the annihilation of positrons: (a) the probability of the formation of positronium, the decrease of which is caused by various inhibition processes, and (b) the rate of destruction of positronium atoms in various interactions with molecules, atoms, radicals, etc. owing to all possible positronium quenching processes.

For laboratory isotope sources of the usual power (up to several hundred millicuries), the steady-state concentrations of positrons or any products of the combination of positrons with electrons, anions, and molecules, do not exceed several units per cm^3. Clearly there can be no question of any classical methods for the observations of chemical reactions involving positronium—it is necessary to employ the experimental techniques of nuclear physics whereby the fate of each individual positronium atom can be followed.

Different arrangements for the measurements are presented in Fig. 2. The top figure shows a triple collision scheme, in which orthopositronium annihilation acts with emission of three γ-quanta incident on $C1$, $C2$, and $C3$ grids, are recorded. A disadvantage of this method consists in the fact that the counting rate $C_{3\gamma}$ of the γ-coincidences is proportional to the product of two variable factors—the probability P of the formation of positronium (the fraction of orthopositronium $I_2 = 3P/4$) and the probability of its spontaneous annihilation (with emission of three γ-quanta), which is $\omega_{3\gamma} = \tau_2/\tau_T^0$, where τ_2 is the

actual lifetime of orthopositronium in the substance, shortened relative to $\tau_T^0 = 1.4 \times 10^{-7}$ s in consequence of various quenching processes. Therefore the decrease of $C_{3\gamma} \propto I_2\tau_2/\tau_T^0$ may be due to both the quenching of positronium (τ_2 decreases) and the inhibition of its formation ($I_2 = 3P/4$ decreases), whereas it is in fact desirable to separate the contributions by these two types of interactions.

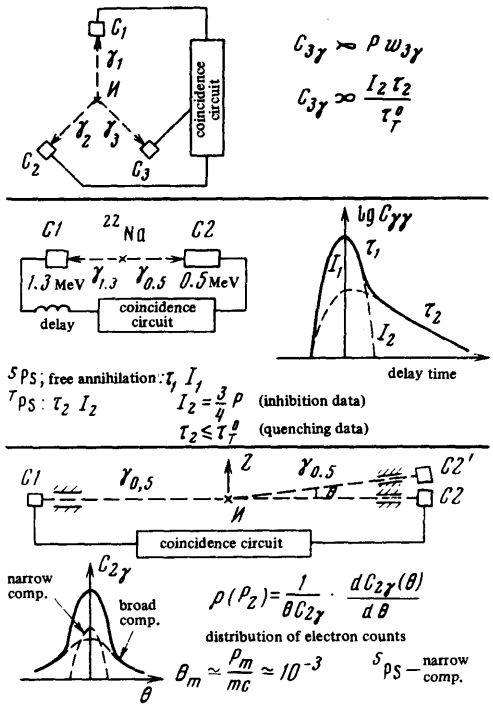


Figure 2. Schematic representation of different procedures for the observation of the fundamental characteristics of the annihilation of positrons. Upper figure—recording of 3γ-coincidences; middle figure—recording of the time spectrum of delayed $\gamma\gamma$-coincidences; lower figure—recording of the angular correlation of the annihilation γ-quanta.

The greatest variety of information is provided by observations of the time spectrum of the annihilation of positrons (the central part of Fig. 2) with the aid of delayed coincidence circuits. The coincidences $C_{\gamma\gamma}$ of the 1.3 MeV nuclear γ-quantum (C1 counter), emitted almost simultaneously with the ejection of a positron from a ^{22}Na nucleus, with the 0.5 MeV γ-quantum (C2 counter) emitted in the 2γ-annihilation of this positron, are recorded. In the simplest case the spectrum consists of two components[38]. The short-lived component with a lifetime τ_1 and a relative intensity I_1 is due to the annihilation of the positron in quasi-free collisions with electrons and in parapositronium and the long-lived component (τ_2, $I_2 = 1 - I_1$) is due to the annihilation of the positrons forming the triplet orthopositronium. The usual order of magnitude of the τ_i in the condensed phase amounts to a fraction of a nanosecond for τ_1 and several nanoseconds for τ_2. In the gas phase τ_2 increases as the pressure is reduced, tending to τ_T^0.

The improvement of the resolving capacity of coincidence circuits made it possible to determine finer details of the time spectra of the annihilation of positrons. Thus four sections of such spectra were observed in the gas phase[39]: an "instantaneous" peak (τ_p) due to the annihilation of parapositronium and the destruction of positrons above the Ore gap, followed by a "shoulder" whose length is inversely proportional to the gas pressure (treated as the lifetime of positrons between emission below the Ore gap and capture), and then sections corresponding to the exponential destruction of positrons with the characteristic annihilation times τ_1 (quasi-free and resonance annihilation) and τ_2 (orthopositronium) (see Fig. 3).

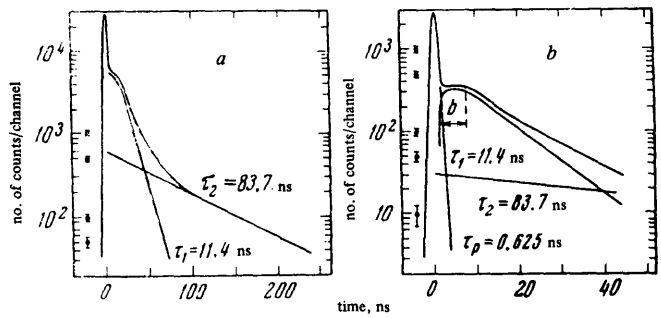


Figure 3. Curves for the distribution of the annihilation of positrons in pure argon with respect to time[39]: *a*) argon pressure 17.2 atm, duration of experiment 1223 min, $\tau_1 = 11.4$ ns, $\tau_2 = 83.7$ ns; b) argon pressure 16.8 atm, duration of experiments 928 min; *b*) width of "shoulder" $\tau_1 = 11.4$ ns, $\tau_2 = 83.7$ ns, $\tau_p = 0.625$ ns—limiting "instantaneous time" accessible to measurement, obtained by the extrapolation of the lifetime of singlet positronium.

For glycerol and many polymers (polyethylene, Teflon, and others) a third component, intermediate between τ_1 and τ_2, was also noted; it is treated here as an effect of annihilation in quasi-free e^+e^- collisions[40].

Finally, in powdered oxides (Al_2O_3, MgO, SiO_2, etc.) the presence of two characteristic long lifetimes—not only τ_2 (several nanoseconds), which is usual for a condensed phase, but also τ_3 (many tens of nanoseconds, up to $\tau_T^0 = 1.4 \times 10^{-7}$ s), caused by the spontaneous annihilation of orthopositronium atoms during their diffusion between the oxide particles, has been established[41-43].

The time method makes it possible to separate clearly the quenching of positronium and the inhibition of its formation. In the simplest case of "pure" inhibition, the intensity of the long-lived component I_2 decreases without further decrease of the slope of its "tail" characterising its lifetime τ_2.

On the other hand, in the case of "pure" quenching, τ_2 falls but I_2 remains unchanged. Two examples taken from Gol'danskii et al.[44], illustrating inhibition and quenching, are presented in Fig. 4, where the distance between two adjacent points in the spectra corresponds to approximately 0.1 ns. Fig. 4*a* illustrates the inhibition of the formation of positronium in benzene by added iodobenzene—probably as a result of positron capture by the iodobenzene—and

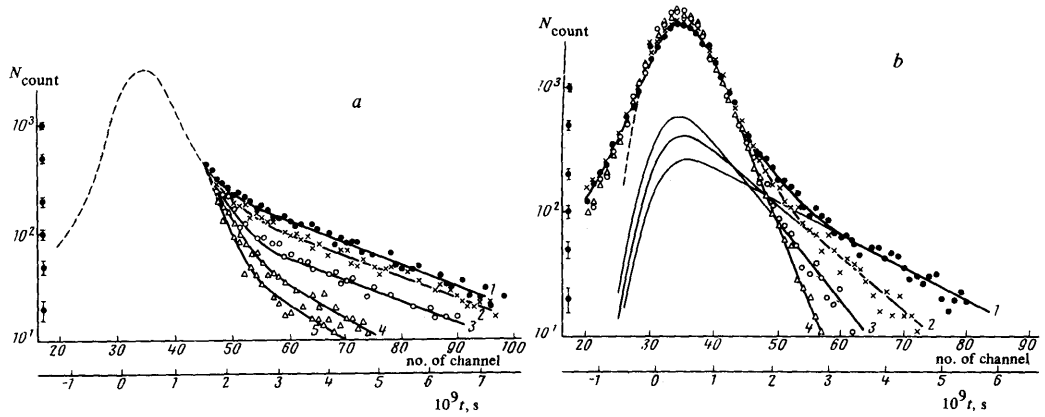


Figure 4. Positron annihilation spectra. *a*: 1) benzene; 2)–4) solutions of iodobenzene in benzene [2) 0.004 M; 3) 0.02 M; 4) 0.34 M]; 5) iodobenzene. *b*: 1) water; 2)–4) aqueous solutions of $K_2Cr_2O_7$ [2) 0.005 M; 3) 0.015 M; 4) 0.025 M]. Power of ^{22}Na source 10 μc.

Fig. 4*b* illustrates the quenching of orthopositronium in aqueous solution by a powerful oxidising agent ($K_2Cr_2O_7$).

The third main experimental method for the investigation of the annihilation of positrons—the observation of correlation curves, i.e. the relations between the counting rate $C_{2\gamma}$ of the coincidence of two 0.5 MeV annihilation γ-quanta and the angle θ, equal to the difference between 180° and the angle between the directions at which the two quanta are emitted—is illustrated schematically in the lower part of Fig. 2. Differentiation ($dC_{2\gamma}/d\theta$) makes it possible to determine the count distribution function for the electrons in the substance. The narrowest component at the angular distribution of the coincidence counting rate $C_{2\gamma}(\theta)$ on the complex correlation curve corresponds to the annihilation of singlet parapositronium. Therefore, by dividing the correlation curves for a series of numerous experiments into narrow and broad components, one can obtain important information, in addition to that from the annihilation time spectra about the chemical reactions of positronium, namely, the contributions by various types of quenching of positronium may be separated. Indeed pick-off annihilation of orthopositronium, as well as the formation of its chemical compounds or oxidation to a positron, correspond to the annihilation of positrons by valence electrons, the kinetic energy of which (T_e) amounts to several electron-volts. Correspondingly, the width of the correlation curves $\Delta\theta \propto \sqrt{T_e/mc^2}$ amounts under these conditions to several milliradians. Nevertheless the ortho-para conversion and subsequent 2γ-annihilation of the slow ^{S}Ps atoms contribute to the correlation curves a central narrow peak near $\theta = 0$, the width of which is about 1 milliradian (the so called narrow component with an intensity I_N). An example of the combination of the time and correlation methods is provided by Fig. 5, where data for aqueous solutions of two manganese salts are presented—the paramagnetic converter $MnSO_4$ and the diamagnetic oxidant $KMnO_4$.[45] The addition of these two salts shortens τ_2, i.e. they behave as quenching agents for positronium. However, the ortho-para converter increases at the same time the intensity of the narrow component of the correlation curve by $\Delta I_N = 15\%$, while the oxidant decreases its intensity by $\Delta I_N = -7\%$, since not only triplet but also singlet positronium is oxidised. The possibility of detecting the oxidation of singlet positronium demonstrates the applicability of positron methods to the observation of reactions occurring over periods as short as 10^{-10} s. A clear confirmation of this possibility is also provided by recent observations of the changes in the intensity of the narrow component ΔI_N for aqueous solution of the $CoCl_2.6H_2O$ converter, the $CuCl_2.2H_2O$ oxidant, and their mixtures[46]. In accordance with the kinetic equations taking into account the oxidation of ^{S}Ps among other processes, the changes in ΔI_N for mixed Co^{2+}–Cu^{2+} solutions are by no means additive relative to the analogous data for Co^{2+} and Cu^{2+} separately (Fig. 6).

The combination of various experimental techniques, supplemented by the variation of a number of parameters (composition, temperature, concentration of additives, and viscosity for liquid systems and composition, temperature, and pressure for gaseous systems) over a wide range makes it possible to verify and analyse in detail different versions of kinetic equations and to determine the kinetic constants for elementary chemical reactions involving positronium.

5. Examples of Information of General Chemical Importance Obtained from Observations on the Annihilation of Positrons

Using various methods described above, the investigators in a number of countries (USSR; USA—Berko, Brandt, Celitans, Lee, McGervey, Tao, and others; Canada—Bell, Hogg, Pohl, and others; France—Paulin and others; India—Thosar and others; Italy—Germagnoli and others; Australia—Green; Norway—Trumpy, etc.) observed fairly numerous examples of all classes of chemical reactions of positronium‡.

Our task is not, however, the description of the chemistry of positronium itself; this new atom is of interest to us as a means of obtaining information of

‡ In the present review we have examined only the reactions of positronium and not the annihilation of slow positrons in general. This is the only reason why we have not mentioned here I. Ya. Dekhtyar, V. L. Fedov, and others (the USSR), de Benedetti, Stewart, Roellig, and others (USA), Massey, Osman, and others (England), Zappa, Colombino, Ferranti, and others (Italy), etc.

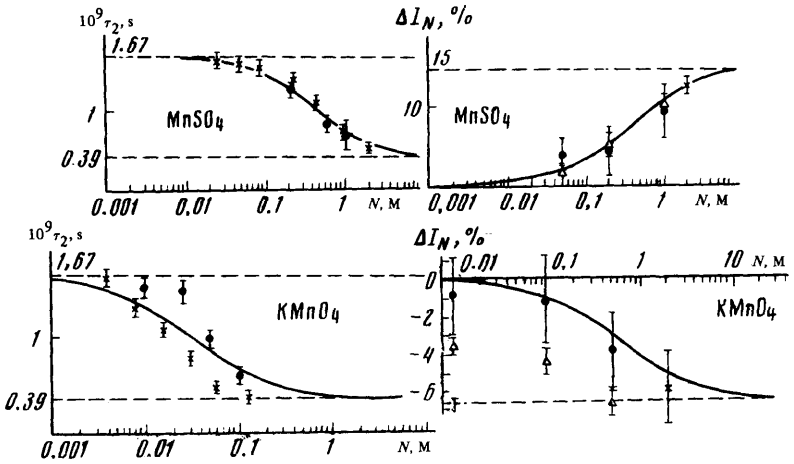


Figure 5. Variation of the lifetime of positrons (τ_2) (on the left) and of the intensity of the narrow component of the correlation curves (ΔI_N) (on the right) in the annihilation of positrons in aqueous solutions of an ortho–para converter ($MnSO_4$; upper figure) and an oxidant ($KMnO_4$; lower figure) as a function of the concentration of additives[1,45]. Power of ^{64}Cu or ^{22}Na source in the experiments on angular correlations—tens of millicuries or several millicuries respectively.

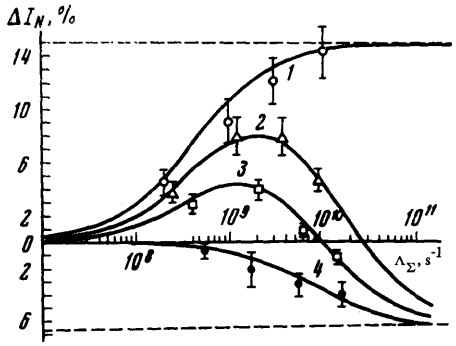


Figure 6. Variation of the intensity of the narrow component of correlation curves in an aqueous solution of converter ($CoCl_2$) and oxidant ($CuCl_2$) salts as a function of the overall rate of conversion and oxidation. Curves *1*–*4* correspond to the contributions by conversion to the overall rates of quenching, which is 100, 80, 50, and 0% respectively, the quenching rate constants being k_{conv} $(2.0 \pm 0.3) \times 10^9$ litre mole^{-1} s^{-1} and $k_{ox} = (5.4 \pm 0.4) \times 10^9$ litre mole^{-1} s^{-1}.

general chemical interest. We shall now consider examples of such information.

In the gas phase the rate of conversion quenching of positronium may serve as a fairly sensitive measure of the concentration of paramagnetic centres—quenching agents. For example, the rate constant for the quenching of positronium by paramagnetic nitric oxide NO, determined by various methods (from annihilation time spectra[28], an increase in the counting rate of the 2γ-coincidences[47], and a decrease in the counting rate of the 3γ-coincidences[48]), amounts to $(1-4) \times 10^{-10}$ cm^3 s^{-1}.

The latest value obtained from observations of the narrowing of the correlation curves is $(2.1 \pm 0.5) \times 10^{-10}$ cm^3 s^{-1}.[49] Adopting this value and assuming that the observation of a change in the counting rate of coincidences by 1% is a real effect, we obtain $n \simeq 10^{13}-10^{14}$ cm^{-3} (at room temperature; with increase of temperature, the sensitivity of the method is unchanged if $\sigma_{conv}v$ = const. and increases when σ_{conv} = const.) as the lower limit of the concentration of the paramagnetic centres recorded in the gas phase by the positron method.

The conversion of positronium includes in all probability the formation of the positronium–converter complex as the first stage. The positronium annihilated in such a complex does not give rise to the narrow component of the correlation curves characteristic of the destruction of free thermalised parapositronium. Therefore the correlation method makes it possible to establish whether the positronium–converter complex became stabilised in new collisions before annihilation or whether the complex decomposed with ortho–para conversion. By varying the concentration of the converter and the overall gas pressure, it is possible to determine on this basis the lifetimes of various positronium complexes; this is important also for other gas-phase reactions. The complexes formed on collision between positronium and NO are very unstable—even at a gas pressure of hundreds of atmospheres they decompose before collision with gas molecules. However, more complicated excited complexes, of the kind of $PsNO_2^*$ or $(CF_3)_2NOPs^*$, which have a larger number of degrees of freedom, have been shown experimentally[50] [for example, by measurement of the correlation curves in argon or oxygen at 30–150 atm with the addition of $5 \times 10^{-4}-0.8$ atm of $(CF_3)_2NO$] to survive for about $(1-2) \times 10^{-12}$ s and to have sufficient time to transfer their excitation energy in new collisions.

We shall now turn to the liquid phase. In the discussion of the mechanism of oxidation–reduction reactions in solutions, the problem of whether an electron is transferred from the reductant to the oxidant by a long-range tunnel transition or via the formation of an intermediate oxidant–reduction complex has been frequently discussed.

In the study of the kinetics of the chemical reduction of anions, Frumkin and coworkers[51] rejected the hypothesis of a long-range tunnel effect. An analogous conclusion was arrived at also on the basis of the comparison of the rate constants for the reactions of hydrogen and positronium atoms with Fe^{2+} and Fe^{3+}, the results of which are presented below (the constants are listed in litre mole^{-1} s^{-1}):

Acceptor	(Ac)	H	Ps	$\frac{k_{Ps}}{k_H}$
$Ac + Fe^{2+}$ →	$[FeAc]^{2+}$	$2 \cdot 10^{7}$ [52]	$2 \cdot 10^{9}$ [54]	100
$Ac + Fe^{3+}$ →	oxidation	$9 \cdot 10^{7}$ [53]	$1.2 \cdot 10^{10}$ [54]	130

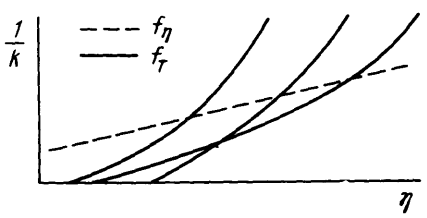
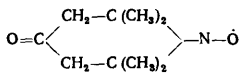


Figure 7. Variation of the reciprocal of the rate constant for the quenching of positronium in the mixed diffusion–kinetic region ($1/k$) with the viscosity of the solution η.[18,55] Dashed straight line—variation of f_η at a constant temperature and a variable solvent composition. Continuous curves—variation of f_T at a constant solvent composition and a variable temperature.

Radiation-chemical studies have shown that the reaction between H and Fe^{2+} proceeds via an intermediate complex, but the mechanism of the reaction between H and Fe^{3+} requires explanation. The fact that the rate of reaction of positronium, which is almost 1000 times lighter, with both Fe^{2+} and Fe^{3+} exceeds to approximately the same extent (by two powers of ten) the rate of reaction of hydrogen suggests that the mechanism of both reactions (with Fe^{2+} and Fe^{3+}) is the same. If a tunnel effect obtained in the second case, there would be no reason to expect such a sharp difference between the rates of the reactions of Ps and H with Fe^{3+}.

Another example of the use of positronium for the investigation of the mechanism of reactions in the liquid phase concerns the development of a method whereby the role of diffusion and kinetic factors can be distinguished[55]. This method, which has been applied to the quenching of positronium, can be readily extended to any other system, which would be of considerable importance to the study of the kinetics of liquid-phase reactions[56].

The method is based on the idea that the viscosity η of a solvent, in which the quenching of positronium by different free radicals [for example, diphenylpicrylhydrazyl (DPPH) $(C_6H_5)_2N-N-C_6H_2(NO_2)_3$ or 2,2,6,6-tetramethyl-4-oxopiperidine 1-oxide



(TMOPO)] takes place, is varied into waves. The viscosity is first increased by altering the composition of the solvent at a constant temperature T_0, for example by adding to water small amounts of glycerol, and then by reducing the temperature ($T < T_0$) for an unchanged composition of the solvent. Under these conditions, the reciprocal of the rate constant for the quenching of positronium ($1/k$) varies as follows:

$$\frac{1}{k} = f_\eta = \frac{\eta}{b}\left(\frac{1}{T_0} + \frac{a'}{\eta\sqrt{T_0}\,P} \cdot e^{E/RT_0}\right)$$

or

$$\frac{1}{k} = f_T = \frac{\eta}{b}\left(\frac{1}{T} + \frac{a}{\eta\sqrt{TP}} e_{E/RT}\right), \qquad (4)$$

where the activation energy E and the solvent parameters b and P are constant and a and a' are very similar. The experiments were carried out in octanol between −12° and 130°C, in ethyl ether between −90° and 25°C, and in cyclohexanol–acetone and water–glycerol mixtures at room temperature. The first type of variation of η is indicated in Fig. 7 by the linear function (dashed straight line) $1/k = f_\eta(\eta)$ while the second type of variation is more pronounced [$1/k = f_T(\eta)$] and is represented by continuous lines. By comparing $f_\eta(\eta)$ and $f_T(\eta)$ and also the slopes of the plots of $\ln k$ and $\ln(1/\eta)$ against $1/T$, it is possible to estimate the activation energy for the quenching of positronium by radicals despite its extemely low value ($E \simeq 1$ kcal mole^{-1}), against the background of the diffusion activation energy $E \simeq 2-6$ kcal mole^{-1}.

To complete the range of examples of the chemical applications of the positronium method in the liquid phase, we shall consider its use in the investigation of the structure of the coordination sphere of the complexes of paramagnetic ions (Co^{2+}) and electron-accepting oxidant ions (Fe^{3+}) in aqueous, alcoholic, and aqueous-alcoholic solutions.

In the first experiments of this kind, the results of which are presented in Fig. 8, the rate of quenching of positronium by the paramagnetic salt $CoCl_2$ (as a result of ortho–para conversion) was compared with the rate of reaction of this salt with TMOPO and DPPH radicals. The quenching was observed from the shortening of τ_2 and the reaction of $CoCl_2$ with the radicals from the broadening of the lines of the radicals in the ESR spectra. The observations were made in propanol, water, and their mixtures of various compositions. A change in solvent composition entails a rearrangement of the structure of the outer coordination sphere of the Co^{2+} complex—the tetrahedral (blue) form $Co(H_2O)_2Cl_2$ characteristics of the alcohol is transformed in water into the octahedral form $[Co(H_2O)_3]\cdot Cl_2$. In this example delocalised unpaired electrons, smeared over the coordination sphere of the complex and concentrated mainly at Cl^- ions in the pure alcohol and at the oxygen atom of the hydroxy-groups in water (the main part of the spin density is of course localised at the Co^{2+} ions themselves, "screened" from positronium by the ligand environment), behave as a quenching agent for positronium (or an agent interacting with radicals). In the mixed solvents the formation of hydrogen bonds between water and the alcohol and also the steric hindrance

due to the propyl radicals in the coordination sphere make the delocalised electron least accessible and retard the reaction of $CoCl_2$ with positronium and other radicals. Fig. 8 shows that under these conditions positronium is in fact the most sensitive detector of changes in the spin density of the delocalised unpaired electron—on passing from propanol and water to their mixtures, the rate of the paramagnetic quenching of positronium falls by a factor of several tens.

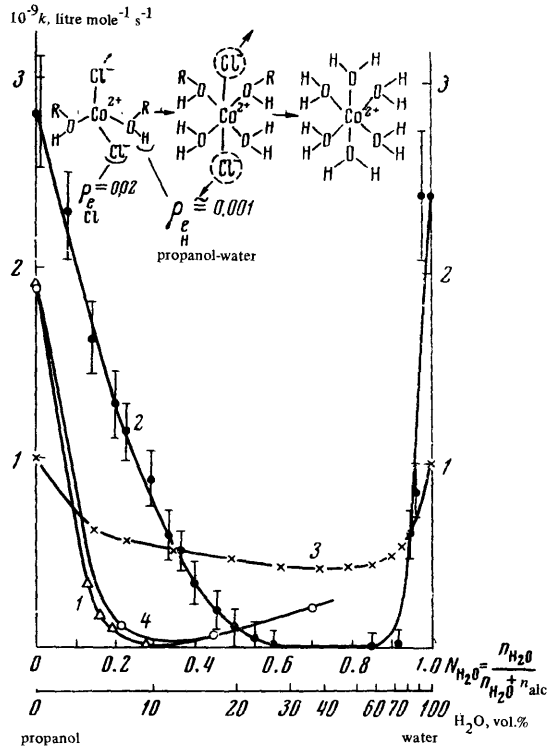


Figure 8. Variation of the rate of reactions of positronium and free DPPH and TMOPO free radicals with the composition of propanol–water mixtures[1,18,57]: 1) concentration of the tetrahedral (blue) form of the complex; sum of concentrations 4.5×10^{-2} M; 2) rate of reaction of Ps with $CoCl_2$ (0.4 M); 3) rate of reaction of TMOPO with $CoCl_2$ (6×10^{-2} M); 4) rate of reaction of DPPH with $CoCl_2$ (4.3×10^{-2} M).

Subsequent experiments on the quenching of positronium by the $FeCl_3$ oxidant in various alcoholic solutions[58] showed that positronium is extremely sensitive also to the delocalisation responsible for the oxidising effect of the Fe^{3+} acceptor orbital.

The observations of a sharp increase in the rate of reaction of positronium with other radicals when solutions are frozen, for example in octanol and benzene[18,59], are very remarkable and hitherto unexplained. For example, the rate of reaction of Ps with TMOPO in frozen octanol at −20°C is higher by a factor of almost 30 than in the liquid at −12°C, i.e. 3 degC above the melting point. These results may indicate both an increase in the rate of diffusion of Ps atoms in the solid phase and the presence of interaction mechanisms specific to the solid state, which operate in the liquid to a much lesser extent and which may play a role not only in the reactions of positronium but in solid-phase reactions in general.

The interpretation of the majority of the data concerning the formation and destruction of positronium in the solid phase is based on the so called "free volume model" examined for the first time by Wallace[60] and developed to the greatest extent by Brandt and coworkers (see, for example, Refs. 61 and 62).

The term "free volume" is applied to all vacancies, defects, and traps and all irregularities in the structure of the crystal lattice where Ps atoms may be located. In the simplest version of the free volume model[60], positronium is distributed in the interstices—a potential well with a periodic inner and exponentially decaying outer wave functions. We have the following quantity normalised to unity:

$$\Psi^2_{\text{outer}} = \frac{k^2/\alpha}{\alpha + \frac{2m_0 u}{\hbar^2} a + \frac{k^2}{\alpha}}, \qquad (5)$$

where

$$\alpha = \frac{\sqrt{2m_0(u-E)}}{\hbar}, \quad k = \frac{\sqrt{2m_0 E}}{\hbar},$$

u is the depth of the well, a its radius, and E the energy of the level occupied by positronium. With decrease of the radius of the well a, i.e. of the free volume, Ψ^2_{outer} increases, which implies an increase in the overlapping of the wave function of positronium with the electron clouds of the surrounding molecules, an increase in pick-off annihilation, and a decrease of τ^2.

In principle it is clear that the changes in free volume must influence not only the lifetime (τ_2) of the Ps atoms in the traps, but also the very probability of the formation of positronium $P = (4/3)I_2$.

Among the factors which may lead to changes in free volume and hence may influence τ_2 and I_2, one must mention in the first place a change in temperature, the contraction of solids, fusion, and various phase transitions[1,62,63].

Having analysed the data for three groups of substances, namely (a) liquids and amorphous materials, (b) polymers, and (c) crystals, Thosar and coworkers[64], concluded that, within the limits of each group, the increase of τ_2 is accompanied by a decrease of I_2, and they obtained the following semiempirical relation:

$$\frac{4}{3} I_2 = a \cdot \frac{1 + \ln \tau_2/\tau_1}{b + \ln \tau_2/\tau_1}, \qquad (6)$$

where

$$a = K\frac{V_f}{v_0}, \quad b = \frac{v_1}{v_0}, \quad \tau_2 = \tau_1 \exp\left(\frac{v - v_1}{v_0 - v}\right),$$

V_f is the overall free volume, and K a constant (Fig. 9).

The significance of Eqn. (6) is that the free volume v corresponding to one positronium atom may vary from $v_{\min} = v_1$ (here $\tau_2 = \tau_1$) to $v_{\max} \to v_0$ (here $\tau_0 \to \infty$) and correspondingly $K = V_f/v$ is in the range $K(v_f/v_0) \leqslant P \leqslant K(V_f/v_1)$. Expressing I_2 as a percentage and τ_2 in nanoseconds, the authors[64] quote the following values of the parameters a and b: $a = 23$ and $b = 0.01$ for liquids, $a = 16$ and $b = 0.01$ for polymers, and $a = 4.5$ and $b = 0.01$ for crystals.

Owing to the different values of the parameter a for the above three groups of substances, the transition from one group to another may involve a change in τ_2 and I_2 in the same direction, for example, in the fusion of naphthalene (the dashed curve N in Fig. 9) or in the crystal–glass transition for Marlex-50 polyethylene (the dot–dash curve M in Fig. 9), where both τ_2 and I_2 increase.

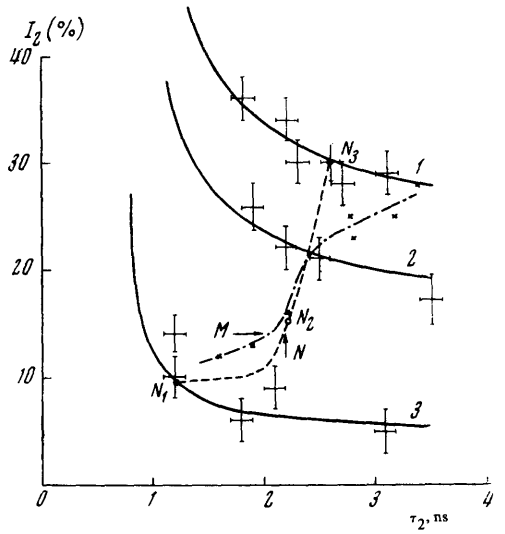


Figure 9. $I_2-\tau_2$ correlation curves for liquid and amorphous materials, polymers, and crystals[64]: 1) liquids and amorphous materials (fused quartz, polystyrene, isopropyl alcohol, liquid naphthalene, benzene, and cyclo-octatetraene); 2) polymers [poly(vinyl chloride), polyethylene, poly(methyl methacrylate), Teflon]; 3) crystals (phenanthrene, naphthalene, stilbene, polyoxymethylene, and Sb_4O_6). N—heating and fusion curve for naphthalene (30 to 80.2°C); M—heating (between −196° and 142°C) and glass-formation curve (−20°C) for crystalline Marlex-50 polyethylene.

The factors which influence the probability of the formation of positronium in solids and its lifetime include also radiation effects and therefore their study must be regarded as one of the promising applications of positron methods.

The after-effects of radiation which may influence the annihilation of positrons are extremely various—they include the appearance of all possible radiation-induced effects (the possibility of the study of which by annihilation methods has been examined[65]), the generation of F-centres to which the annihilation of positrons proved to be extremely sensitive[24], the formation of ions and paramagnetic centres, etc.

The first experiments on the influence of radiation on the characteristics of the annihilation of positrons were performed as early as 1957–1958.[56] Subsequently it was shown that, as a result of the irradiation of solid anthracene with neutrons, positronium begins to form, as in liquid anthracene and in contrast to non-irradiated crystals, both τ_2 and I_2 increasing with radiation dose[67], although τ_2 does not in fact reach the value characteristic of liquid anthracene.

The wide variety of the effects of radiation is shown, for example, by the fact that, following the γ-irradiation of Teflon, the opposite behaviour is observed—τ_2 and I_2 decrease with radiation dose[68,69], which has been attributed to the increase of the degree of crystallinity of Teflon on irradiation and the quenching of positronium by the free radicals formed.

Indeed it has been shown[65] that the variation of τ_2 in the γ-irradiation of Teflon is correlated with the radical concentration determined by ESR. At the same time, according to the data of Indian investigators, the breakdown of the microcrystals and the increase of the proportions of low-density amorphous regions in irradiated polyethylene lead to an increase of τ_2,[70] while the rupture of benzene rings in polystyrene on neutron irradiation leads to a decrease of I_2,[71] since the formation of positronium in compounds of this kind is in fact mainly localised at aromatic rings.

Recently the positron method was applied in Japan (Tabata and coworkers[19,72]) in observations on radiation-induced solid-phase polymerisation of a number of monomers (acrylonitrile, methacrylonitrile, acetaldehyde, N-vinylcarbazole, and dimethyl and diethyl itaconates).

A number of factors influencing the formation and destruction of positronium arise in the course of polymerisation. As the polymeric chain grows, the number of defects and dislocations in the crystalline monomer increases—the systems of monomeric units contract after polymerisation. All these factors are responsible for a general increase in free volume, which alone would lead to an increase of τ_2. At the same time, the presence of terminal active centres (usually paramagnetic) of the growing polymeric chains at the free volume boundaries is responsible for a multiplicity of ways in which positronium can be destroyed and thus shortens its lifetime—together with pick-off annihilation there is the possibility of ortho–para conversion and positronium capture. Ultimately fairly different types of relation between τ_2 and I_2 may arise. With increase of radiation dose D from 5 to 20 Mrad, a correlation similar to that described by Thosar et al.[64] is observed for N-vinylcarbazole—initially τ_2 increases and I_2 falls and then (starting with $D \simeq 13$ Mrad) the opposite variation is observed, τ_2 decreasing and I_2 increasing. On the other hand, in dimethyl itaconate an increase of the degree of polymerisation is accompanied by an appreciable increase of the probability of the formation of positronium (Fig. 10), while τ_2 remains almost constant.

Apart from radiation-induced polymerisation, the positron method has recently been applied for the first time to another kinetic problem in polymer chemistry, namely in the study of the ageing of poly(vinyl chloride) due to thermal oxidation[73]. Prolonged heating of this polymer leads to a sharp reduction of τ_2, while I_2 increases with temperature. In the vicinity of the phase transition of the polymer at 195°C, τ_2 passes through a minimum ($\tau_2^0/\tau_2 \simeq 3$) and I_2 passes through a very sharp maximum ($I_2/I_2^0 \simeq 2$, where τ_2^0 and I_2^0 correspond to room temperature). The decrease of τ_2 was compared with the accumulation of free radicals detected by ESR and with the weight loss by the polymer owing to the elimination of HCl. The clear correlation between the above quantities has been interpreted[73] as confirmation of the mechanism of the quenching of positronium by combination with radicals or double bonds, or by ortho–para conversion, or finally by the interaction of Ps with HCl or HCl_2^-.

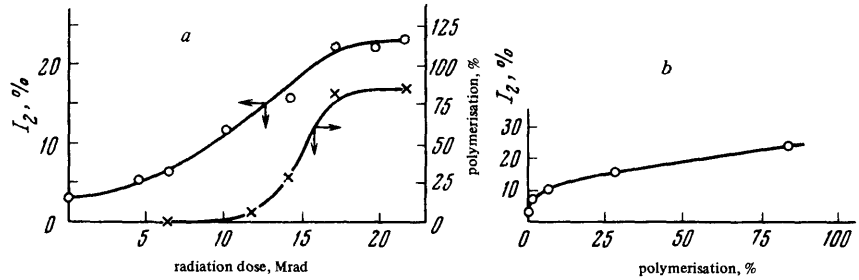


Figure 10. *a*) Variation of I_2 (%) and percentage polymerisation with radiation dose (^{60}Co γ-radiation) in the radiation-induced solid-phase polymerisation of dimethyl itaconate[69]; *b*) variation of I_2 with percentage polymerisation of dimethyl itaconate[69].

Thus the first, not altogether fully defined possibilities of the new chemical applications of positron methods have been outlined, namely in observations on the kinetics of solid-phase reactions accompanied by marked changes in the structure of the solid.

6. Characteristics of the Annihilation of Positrons in Porous Media

In conclusion of the section on positronium, we shall consider the most interesting observations on the characteristics of the annihilation of positrons in highly dispersed media and the wide variety of prospects for the employment of the results of these observations.

As already mentioned, in the study of the positron annihilation spectra in powdered oxides (Al_2O_3, MgO, SiO_2), Paulin and Ambrosino[41] observed two long-lived components—with a lifetime τ_2 of the order of several nanoseconds, characteristic of pick-off annihilation in the solid, and τ_3 of the order of several tens of nanoseconds, up to $\tau_T^0 = 1.4 \times 10^{-7}$ s. With increase of the degree of dispersion of the powders, i.e. with increase of the proportion of free volume $v_f/v = (\rho_0 - \rho)/\rho_0$ (ρ_0 is the density of the monolithic substance and ρ its density), an increase was observed in the intensity of the most long-lived component I_3 owing to the decrease of the contribution by the pick-off component I_2. An example is provided by Table 1.

The τ_3 component arises as follows. The positrons retarded in the porous solid can ultimately form Ps atoms. Part of these atoms undergo pick-off annihilation in the solid itself, while others emerge into the free volume between the particles. The probability of the capture of such atoms on impact against the surface of the particles is very low—they are much more likely to undergo repeated reflection (albedo) being ultimately destroyed in the pore volume (in flight)—either by pick-off annihilation in the pores filled with gas or in consequence of spontaneous annihilation. The relative contributions of these two processes may be assessed from the fact that the value of τ_3, reaching 140 ns in a vacuum, decreases by a factor of 2 when experiments with SiO_2 are performed in air or oxygen at the normal pressure.

Brandt and Paulin[42] calculated from the data of Paulin and Ambrosino[41] the characteristics of the diffusion of Ps atoms in the particles of solid oxides—the diffusion coefficients in the range between $D = (5.8 \pm 1.9) \times 10^{-5}$ (SiO_2) and $D = (1.4 \pm 0.7) \times 10^{-3}$ (MgO) cm^2 s^{-1}, the activation energy for diffusion $E = 700 \pm 370$ cal mole^{-1}, and the overall paths traversed before annihilation $\lambda = \sqrt{2D\tau}$ (46 ± 7 Å in SiO_2 and 270 ± 80 Å in MgO—for orthopositronium). Apart from the powdered oxides enumerated above, Bartenev et al.[43] observed the τ_3 component also in powdered BeO but not in the sintered oxide. Observations on the angular correlation of the annihilation quanta demonstrated the presence of a narrow component in BeO, MgO, SiO_2, and Al_2O_3 powders and its absence in monolithic specimens of these oxides. One cannot rule out the possibility that the results of the above investigations[41-43] explain the high probability of 3γ-annihilations in certain alkali metal halides and particularly in BeO and MgO, discovered and investigated by Italian workers[74,75] (see also Refs. 1 and 63), which for a long time appeared to be a puzzling anomaly. In all probability, these findings are not due to the molecular properties of the materials investigated but to their high degree of dispersion—indeed the entire anomaly in the counting rate of the 3γ-coincidences for MgO disappeared on passing to single crystals[76].

Table 1. Characteristics of the annihilation of positrons in highly dispersed oxide powders.

Substance	Specific surface m^2 g^{-1}	ρ, g cm^{-3}	τ_2, ns	I_2, %	τ_3, ns	I_3, %
SiO_2	50	0.3	1.77±0.2	28±2	140±4	4±0.5
SiO_2	180	0.06	1.89±0.2	10.7±0.8	142±3	11.6±1
SiO_2	300	0.05	2.1±0.2	4.5±1	132±3	12±1
SiO_2	380	0.05	3.4±0.4	4±1	137±3	15±1
Al_2O_3		1	3.6±0.4	2.5±1.5	87±3	15.7±1
MgO		0.35	2.9±0.3	1.8±1.5	126±3	25.6±2

The extension of the range of substances investigated by positron methods in a highly dispersed state constitutes an urgent problem. Possibly the formation of positronium in fine-pored specimens will be detected also in substances where its existence has been hitherto ruled out—for example, metals.

Other consequences of the above studies[41-43] are also of interest—the observations of the reactions of positronium with atoms and molecules adsorbed on surfaces or

filling adsorbent pores and the development of positron methods for the investigation of the physical chemistry of surface phenomena, adsorption, and heterogeneous catalysis are promising.

The probability of the capture of hydrogen atoms (ϵ_H) on impact against various surfaces is known to vary within extremely wide limits—from $\epsilon_H = 10^{-4}-10^{-5}$ for SiO_2 to $\epsilon_H \simeq 1$ for graphite and $ZnO.Cr_2O_3$.[77] Moreover, ϵ_H depends markedly on temperature: $\epsilon_H \propto \exp(-E/RT)$, where $E = 9000-13\,000$ cal mole^{-1}.

There is reason to expect similar relations also for positronium and comparison of data for positronium, with its exceptionally low mass and large de Broglie wavelength, and hydrogen is of particular interest.

The interest becomes even greater in connection with the recent theoretical demonstration by Kagan[78] that a neutron can also give rise to a long-lived bound state in porous substances: the porous medium behaves as a kind of "sponge" which sorbs neutrons into a bound state with a binding energy of the order of 10^{-7} eV and a characteristic lifetime, which reaches tens and hundreds of seconds at the helium temperature.

The annihilation spectra of positrons in silica gel, alumina gel, and aluminosilicate catalyst specimens of moderate porosity, having specific surfaces in the range 130–230 m^2 g^{-1} and an average pore radius of about 40 Å, were recently compared[79] at a number of points on the water desorption isotherm at room temperature. As long as the water vapour pressure p is close to the saturated vapour pressure p_S ($p/p_S \gtrsim 0.3$), the τ_3 component in the time spectra is altogether absent, since the pore volume is entirely filled by liquid water. On the other hand, in the region of low values of p/p_S, corresponding to a more or less depleted monolayer of physically adsorbed water, a correlation was noted between the catalytic activity of the specimens in the dealkylation of cumene (i.e. the strength of the Brönsted acid centres) and the values of τ_3. For catalytically inactive silica gel and alumina gel, the desorption of water with decrease of p/p_S hardly affected τ_3, while for the aluminosilicate catalyst τ_3 decreased appreciably under these conditions, apparently due to the reaction $H^+ + Ps \rightarrow H + e^+$, which is energetically possible only for non-hydrated protons weakly bound to the surface of the pore, i.e. only for strong proton acid centres. The effect of the desorption of water on τ_3 in the region of low values of p/p_S for catalyst specimens containing sodium cations was much weaker and the values of τ_3 themselves were higher. Indeed the reaction $Na^+ + Ps \rightarrow Na + e^+$ is endothermic ($Q = -1.63$ eV) and therefore it could not play an appreciable role. Thus a change in the probability of the capture of positronium ϵ_{Ps} as a function of the state of the surfaces of adsorbents and catalysts was demonstrated[79].

The observation of the annihilation of positrons in porous materials in an atmosphere of different gases is frequently more convenient than experiments with the gases themselves—the volume of the highly dispersed system necessary for the effective retardation of positrons is much smaller than for pure gases and the positronium atoms traversing the labyrinth between the grains of the highly dispersed powders do not leave the field covered by the counters recording the annihilation γ-quanta up to the very instant of annihilation.

These advantages were fully reflected in the work of Chuang and Tao[80], who observed the annihilation of positrons in iodine and carbon tetrachloride adsorbed on silica gel. In our remark in subsection 4 that a decrease of I_2 for a constant value of τ_2 corresponds to "pure" inhibition of the formation of positronium and a decrease of τ_2 for a constant I_2 corresponds to its "pure" quenching, we simplified the situation somewhat.

If fast positronium atoms enter into an endothermic threshold reaction, which is possible only up to their retardation and "thermalisation" and leads to instantaneous annihilation, the annihilation spectrum shows an additional component with a short lifetime virtually indistinguishable from τ_1. The conversion of some of the orthopositronium atoms into this component is detected as a decrease of I_2—in other words the quenching of fast Ps atoms is recorded as apparent inhibition. This type of apparent inhibition, due to the reaction $Ps + Cl_2 \rightarrow PsCl + Cl$, was in fact observed by Tao[81] after the addition of chlorine to argon. The possibility of distinguishing true quenching agents and inhibitors on the basis of their influence on annihilation in the adsorbed state has been demonstrated[80]. The authors[80] believe that the adsorption of the quenching agent on the surface of silica gel alters significantly the potential for the interaction of Ps with the surface or, using the terminology adopted above, by increasing the probability of the capture of positronium ϵ_{Ps} it thereby shortens τ_3. At the same time the adsorption of the quenching agent should lower also the value of I_3, since the presence of the quenching agent on the surface of the adsorbent reduces the probability of the liberation of Ps atoms from the bulk of the silica gel globules into pores. Both these effects, the decrease of τ_3 and I_3 with increasing amount of the adsorbed substance, have been observed for iodine, which is therefore believed[80] to be a true quenching agent for positronium. Different results have been obtained for the "pseudoinhibitor" carbon tetrachloride—over a wide range of its concentrations (up to the saturation of a monolayer on the surface of silica gel), I_3 decreased, while τ_3 remained unchanged. This implies that the presence of carbon tetrachloride on the silica gel surface does not increase ϵ_{Ps}.

The total experimental data obtained by Paulin and Ambrosino[41] and subsequent investigators for the annihilation of positrons in porous media and also the relevant theoretical considerations indicate the possibility of creating effective highly dispersed positronium sources (it must be stressed that these are in fact positronium sources and not simply positron sources), which are particularly promising for the study of chemical reactions in gases over a wide range of temperatures and pressures.

III. MUONIUM

1. The Nuclear-physical Characteristic of the μ^+-Meson and Muonium

Muonium (atomic system consisting of a μ^+-meson as the central nucleus and an electron) is a hydrogen-like atom—a model light analogue of atomic hydrogen. The μ^+-meson (an elementary particle) (mass 206.76 $m_e \simeq \frac{1}{9} m_p$; lifetime with respect to the decomposition into a positron, a neutrino, and an antineutrino 2.2×10^{-6} s; spin 1/2; magnetic moment 8.89 nuclear magnetons) arises in the decomposition of π^+-mesons formed in charged-particle accelerators as a result of nuclear reactions above the meson generation threshold. It is significant that in the decomposition of π^+-mesons in flight the resulting μ^+-mesons are fully polarised longitudinally in consequence of the non-conservation of parity in the $\pi\mu e$ decomposition,

i.e. the spin of the ejected μ^+-meson is oriented in opposition to the direction of its motion. The ejection of the position in the μe decomposition ($\mu^+ \rightarrow e^+ + \nu + \tilde{\nu}$) takes place preferentially in the direction of the spin of the meson and there is a steric asymmetry with the impulse of the positron.

In the theory of the two-component neutrino[82-84], the asymmetry coefficient c, defined as the ratio of the difference between the "forward" and "reverse" decompositions (along and in opposition to the initial direction of the spin of the μ^+-meson) to their sum, averaged over the entire energy spectrum of the decomposition positrons, is 1/3 (polarisation $P = 1$) for fully polarised μ^+-mesons. The change in the polarisation of μ^+-mesons in the medium as a function of the experimental conditions is a characteristic of the interactions with matter.

When the meson is retarded to velocities of the order of that of atomic electrons of the medium, a charge-transfer stage ensues, which is completed by the capture of an electron and the formation of a stable μ^+e^- atomic system, i.e. a muonium atom (ionisation potential 13.539 eV, Bohr radius 0.532 Å, mass $207.76m_e$). Since the initial direction of the spin of the μ^+-meson is arbitrary, the formation of muonium with parallel and antiparallel orientations of the meson and electron spins is equally probable (the $^3S_1$, $m = 1$ triplet state with a population of 1/2 and superposition of the $^1S_0$, $m = 0$ and $^3S_1$, $m = 0$ states with populations of 1/4 in each case). In the first case the spin of the μ^+-meson in the absence of external perturbations retains its initial polarisation in the course of the lifetime of the meson; in the second case there are harmonic oscillations between the (1,0) and (0,0) states, the frequency of which (ω_0) is determined by the hyperfine splitting energy ΔW ($\omega_0 = \Delta W/\hbar = 2.804 \times 10^{10}$ s^{-1}). Thus in a period of the order of about 10^{-10} s the para-state of muonium undergoes irreversible depolarisation and the overall asymmetry coefficient decreases to the level of 1/2 of the initial value. Processes involving the exchange of electrons having opposite spins with the medium (conversion) can lead to further depolarisation of the μ^+-meson down to zero.

We may note that the "thermalisation" time of the μ^+-meson in condensed media and gases at a pressure greater than 50 atm does not exceed $10^{-12}-10^{-13}$ s, which is significantly less than the characteristic depolarisation time ($1/\omega_0$). Consequently depolarisation during the retardation time is insignificant; repeated charge transfers in the inhibition of the meson do not lead to a change of its spin and the probability of the formation of the ortho- or para-state of muonium depends only on the last electron capture step.

In fairly strong longitudinal (in the direction of the spin of the μ^+-meson) external magnetic fields, the interaction of the magnetic moments of the meson and the electron in the muonium atom disappears; both populated states (+1/2, +1/2 and 1/2, −1/2) retain the initial polarisation of the μ^+-meson. A critical condition for which the magnetic energy of muonium in the external magnetic field is equal to the hyperfine splitting energy is that $H_0 = \Delta W/2(\mu_e - \mu_\mu) = 1585$ G. Since ΔW depends on the cube of the distance between the interacting magnetic moments [$\Delta W = f(r^{-3})$], it is clear that H_0 is extremely sensitive to changes in the distribution of electron density in the molecule incorporating muonium. The last factor allows an additional identification of the form in which muonium is present in the medium. In transverse magnetic fields there is a Larmor precession of the spin (or a system of spins) with a frequency determined by the magnetic moment and the spin. Since the magnetic moment in the triplet state of muonium is determined largely by the magnetic moment of the electron and the spin is unity, the precession frequencies of the μ^+-meson and triplet muonium differ by a factor of about 103 and can be readily distinguished experimentally.

A typical apparatus for the measurement of the asymmetry coefficient for the angular distribution of μe-decomposition positrons (Fig. 11*a*) incorporates two telescopes comprising two scintillation counters, each recording the passage of charged particles. The arrest of a μ^+-meson by the target *5* is recorded by the counters *1* and *2* in the absence of coincidences with the counters *2* and *3*, giving rise to a "start" pulse signal. In the decomposition of a μ^+-meson on the target, positrons are recorded by the counters *3* and *4*, giving rise to a "stop" signal in the absence of coincidences with the counters *2* and *3*. The pulses produced according to the $12\overline{23}$ and $34\overline{23}$ scheme control the operation of the time–amplitude converter.

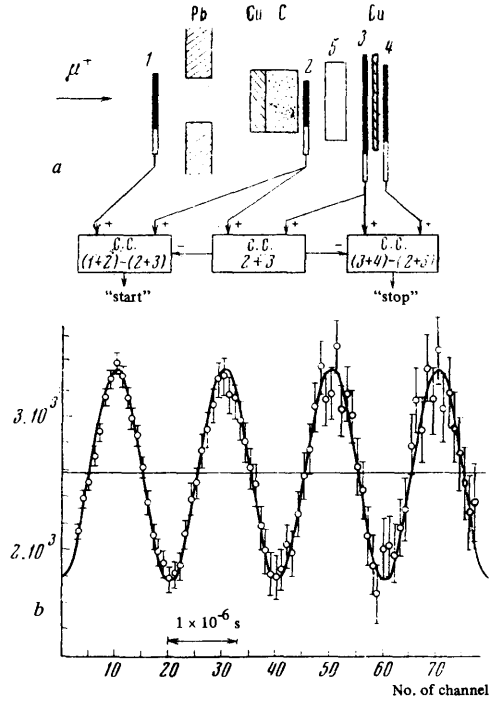


Figure 11. *a*) A typical arrangement of the apparatus for the measurement of the asymmetry coefficient for the angular distribution of μe decomposition positrons [1)–4) scintillation counters; 5) target; C. C.—coincidence circuits]. The magnetic coils are not shown in the Figure. *b*) The precession curve in bromoform. The numbers of readings in the channels are corrected for the background and the exponential decomposition of μ^+-mesons.

The latter transforms the time interval between the pulses into a variable amplitude signal recorded by a multichannel analyser. The use of a transverse magnetic field of the required strength leads to the modulation of the exponential decomposition curve for the Larmor precession of the μ^+-meson or triplet muonium. After the correction of experimental data for the random coincidence background and the decomposition of the μ^+-meson, a

typical precession curve has the form shown in Fig. 11*b* (in this case the magnetic field strength was 50 G and the precession period about 1.5×10^{-6} s).

2. Physicochemical Principles of the Interactions of Muonium

a. Kinetic scheme. Calculation of the rate constants for the chemical reactions of muonium. In the majority of cases the behaviour of muonium (Mu) described is complicated by its involvement as a hydrogen-like atom in chemical reactions with the molecules of the medium, with formation of fairly strong chemical bonds in a manner analogous to the reactions of atomic hydrogen. In view of their wide occurrence, the reactions of atomic hydrogen have been investigated in detail by chemical kinetic methods in the course of several decades (see, for example, the relevant fundamental monographs[85,86]).

The incorporation of muonium in the molecule after chemical reaction alters fundamentally the factors governing its depolarisation in the medium[87,88]. In the reaction with an unsaturated covalent compound (for example, $C_8H_{18} + H \rightarrow H_2 + C_8H_{17}^{\cdot}$; the dot designates the unpaired electron of the radical product), which is typical for atomic hydrogen, the hydrogen atom enters into the composition of a molecule with a closed diamagnetic shell, where the electron spins are compensated in pairs. A similar reaction involving muonium has the same consequences. Thus the magnetic field created by electrons at the point where the μ^+-meson is located in the molecule is zero. Under these conditions, there is no coupling of the magnetic moments of the meson and the electron and depolarisation by the above process does not occur. However, the interaction with the magnetic moments of the adjacent nuclei of the molecule is possible, provided of course that the latter are not even–even. Under real conditions, allowance for the rotational states of molecules, in particular for gases and liquids, leads to a virtually negligible contribution by depolarisation factors to the formation of the diamagnetic electron shell; for solids, this depolarisation mechanism can play an appreciable role only when $r \lesssim 1$ Å.

It is significant that the Larmor precession for muonium incorporated in the molecule occurs at a frequency corresponding to a free μ^+-meson. Indeed the absence of magnetic interactions between the meson and the electrons of the diamagnetic shell of the molecule corresponds to an independent interaction of the magnetic moment of the μ^+-meson with the external field. This factor resolves the apparent contradiction in the earlier experimental studies, where the search for the precession of triplet muonium was unsuccessful, but the precession of the spin of the μ^+-meson was observed[89,90].

Thus the involvement of muonium in the composition of a diamagnetic molecule leads to the "freezing" of the depolarisation processes at a level which depends on the rate of reaction of muonium with the medium. For a fairly short characteristic time of the chemical reaction τ, the para-state of muonium (Mu^S) is involved in the process, which prevents depolarisation when $\tau \ll 1/\omega_0$; then precession at the frequency of the free μ^+-meson (the meson component) has the maximum amplitude. With increase of τ, there is a possibility of partial or complete depolarisation of Mu^S; the probability of the reaction of triplet muonium (Mu^T) and Mu^S which has retained its polarisation corresponds to the observation of the meson precession with an amplitude depending on the value of τ. Finally, for large values of τ (for example, $\tau > \tau_{\mu^+}$), the absence of chemical interactions makes it possible to observe the precession of the frequency of triplet muonium (the muonium component). Consequently, a qualitative treatment yields the relation between the rate of the chemical reaction of muonium and the experimental polarisation at the corresponding (meson or muonium) frequency. We may note that, in the absence of conductivity electrons, the conversion exchange is appreciably suppressed, since it apparently requires an energy expenditure on the scale of the triplet excitation energy of molecules and for covalent compounds the rate of such exchange does not exceed the rate of decomposition of the μ^+-meson.

We shall now formulate the characteristics of the muonium method for the investigation of chemical processes. Firstly, one of the characteristic conditions associated with the specific features of the experimental method is the presence throughout the bulk of the test substance only of single muonium atoms. Thus the reaction kinetics are studied in the initial stage when there are no complications associated with the formation and accumulation of secondary reaction products in the bulk phase. Secondly, the use of nuclear-physical constants as independent time standards permits the determination of the absolute rate constants for a wide range of fast reactions. Thirdly, the observation of the behaviour of the spin and the magnetic moment of the μ^+-meson allows the study of the factors determining the spin interactions during the process or at steady state, which is one of the unique characteristics of the method. Fourthly, the typical independence of the recording method of the external experimental parameters significantly increases the scope of the investigation; in particular, the method becomes universally applicable to various states of aggregation of matter.

From the standpoint of the experimental characteristics associated with the method (the observation of the meson and muonium precession frequencies in an external magnetic field), it is desirable to classify in appropriate groups the products obtained as a result of the reaction. We shall include in the first group molecules which incorporate muonium and have a diamagnetic electron shell; the second group includes reaction products with an unpaired electron (radicals). In the absence of an effect of the magnetic moments of the surrounding nuclei, the products of the first group are observed at the meson frequency. We may note that, in the reaction of muonium with a molecule having different substituents, parallel pathways are possible, but, since the molecular products are indistinguishable in terms of experimental technique (in the concrete example of the interaction of muonium with chloroform, MuH and MuCl are formed, the precession occurring at the meson frequency in both cases), the probability of the formation of the sum of the molecular products is determined. In the formation of radical products incorporating muonium (for example in the reaction involving addition to a multiple bond: $Mu + H_2C = CH_2 \rightarrow H_2MuC-CH_2^{\cdot}$), the interaction of the magnetic moments of the μ^+-meson and the unpaired electron (complicated by the change of the average effective distances and the nature of the delocalisation of the electron in the molecule) persists. In this case there is no precession at the meson frequency, but the "latent" polarisation may be determined either from its restoration in longitudinal magnetic fields in consequence of a change in H_0 or from the competition between various reactions of muonium in

homogeneous mixtures of compounds (the method of competing acceptors).

We shall now consider a kinetic scheme for the reactions of muonium with matter[88,91]. The time interval between the individual steps involving the entry of a μ^+-meson into the space occupied by the test compound is much longer than its lifetime. Consequently the number of mesons in the system is unity (the time interval between the decomposition of a μ^+-meson and the entry of the next particle is insignificant, since no processes occur during this interval) and the statistical conditions for a steady state are fulfilled; the rates of appearance and loss of reaction intermediates are then equal. In the general case it is necessary to take into account the following competing processes: reactions with formations of molecular and radical products, reactions involving conversion spin exchange with the electrons of the molecules of the medium, irreversible depolarisation of Mu^S in consequence of spin flip, and the decomposition of the μ^+-meson. We may note that any chemical reactions of a depolarised muonium atom (Mu^D) naturally yield products with an isotropic angular distribution of decomposition positrons. The interaction of muonium with hydrogen-containing compounds can be formulated schematically as follows:

$$\begin{aligned}
&(1).\ Mu^T\ (Mu^S) + RH \xrightarrow{k_1} MuH + R^{\cdot}\ ,\\
&(2).\ Mu^T\ (Mu^S) + RH \xrightarrow{k_2} RMuH^{\cdot}\ ,\\
&(3).\ Mu^T\ (Mu^S) + RH \xrightarrow{k_3} Mu^S\ (Mu^T) + RH\ , \qquad (1)\\
&(4).\ Mu^S \xrightarrow{k_4} Mu^D\\
&(5).\ Mu^T\ (Mu^S, MuH, RMuH^{\cdot}, Mu^D) \xrightarrow{k_5} e^+ + \nu + \tilde{\nu}\ .
\end{aligned}$$

By fitting the function $\exp(-\lambda t)$ to the average polarisation of Mu^S ($1/\omega_0 t.\sin\omega_0 t$), we find the depolarisation rate constant $k_4 = \frac{2}{\pi}\omega_0$; the decomposition rate constant is $k_5 = 1/\tau_{\mu^+}$.

Using the method of steady states, we obtain expressions relating the rate constants for reactions (1)–(5) to the experimental asymmetry coefficients c_1', c_2', and c_3' determined under various conditions:

$$\frac{2k_5 + 2(k_1+k_2)[RH]}{k_4}\cdot\frac{1}{1+\dfrac{2k_3[RH]}{(k_1+k_2)[RH]+k_5}} = \frac{c_1'}{fc-c_1'}\ , \qquad (2)$$

$$\frac{k_1[RH]}{k_2[RH]+k_5+\dfrac{k_4}{2+\dfrac{k_4}{(k_1+k_2)[RH]+2k_3[RH]+k_5}}} = \frac{c_2'}{fc-c_2'}\ , \qquad (3)$$

$$\frac{k_2[RH]+k_5}{k_1[RH]+\dfrac{k_4}{2+\dfrac{k_4}{(k_1+k_2)[RH]+2k_3[RH]+k_5}}} = \frac{c_3'}{fc-c_3'}\ , \qquad (4)$$

where f is the degree of polarisation of the initial beam of μ^+-mesons, which depends on the kinematic conditions of the formation of the meson beam in accelerators. Formula (2) corresponds to the case where the depolarisation of the μ^+-meson is due solely to reaction (4) and characterises the overall reactivity of the compound via all reaction pathways. Formulae (3) and (4) are applicable to experiments by the precession method in transverse magnetic fields and describe the meson and muonium components respectively. We may note that, for reaction rates comparable to ω_0, the inaccuracy of the approximation employed for the average polarisation of Mu^S limits the applicability of the formulae. In this case it is necessary to take into account the oscillatory nature of the depolarisation of Mu^S when reactions (3) and (5) are neglected owing to their small contributions[92].

The statistical accuracy of the determination of the absolute rate constants for the reactions of muonium depends on the magnitude and accuracy of the determination of the asymmetry (polarisation) coefficients. The current experimental techniques ensure an accuracy in the determination of the reaction rate constants for a pure compound reaching under favourable conditions 10–20%.

Table 2. Rate constants for the reactions of muonium.

Compound	Formula	k_1	k_2
Cyclohexane	C_6H_{12}	$(2.4\pm0.2)\cdot10^9$	—
Methanol	CH_3OH	$(5.6\pm1.1)\cdot10^8$	—
Octane	C_8H_{18}	$(2.9\pm0.4)\cdot10^9$	—
Chloroform	$CHCl_3$	$(4.2\pm1.4)\cdot10^9$	—
Benzene	C_6H_6	$(3.0\pm1.1)\cdot10^8$	$(3.1\pm0.4)\cdot10^9$
Bromoform	$CHBr_3$	$(1.1\pm0.2)\cdot10^{10}$	—
Diphenylpicrylhydrazyl (DPPH)		$(7.6\pm2.2)\cdot10^{10}$	

With a correct choice of the second solution component, the method of competing acceptors makes it possible to obtain the maximum accuracy in all necessary cases; moreover, this method allows the detection, from the results of the measurements of the meson frequency, of radical product formation processes.

b. Experimental data for a number of compounds. We shall examine one specific example[92,93] the determination of the absolute rate constants for the reaction of muonium by the method of competing acceptors. In order to observe the precession in a transverse magnetic field at the meson frequency, measurements were made of the asymmetry coefficients for individual substances (listed in Table 2) and their binary solutions. Some of the data obtained for the variation of the asymmetry coefficient with the concentration of the substance in solution are presented in Fig. 12. We may note that for heterogeneous mixtures, where the competition between parallel reactions is appreciably suppressed, or in the absence of chemical interactions, the dependence of the asymmetry coefficient on the concentration of the mixture components should be linear, while for competing acceptors the form of the analogous relation is determined by the ratio of the overall (via pathways involving the formation of both molecular and radical products) reactivities of the compounds. The curve for $C_6H_6-CHBr_3$ is typical in this sense (Fig. 12*a*).

The form of the curve for the $C_6H_6-CH_3OH$ mixture is important (Fig. 12*b*)—despite the lower asymmetry coefficient at the meson frequency for benzene, the overall consumption of muonium in the interaction with benzene is higher than in the interaction with methanol, which leads to a deviation of the curve relating the asymmetry coefficient to concentrations towards smaller values. This is evidence of the predominance of the "latent" polarisation due to the radical pathway of the reaction of muonium with benzene involving the formation of $C_6H_6Mu^{\cdot}$.

Quantitative calculation for the system as a whole yielded the reaction rate constants (in litre $mole^{-1}$ s^{-1}) listed in Table 2. These data may be used to calculate the

rate constants for the corresponding reactions of atomic hydrogen, provided that the activation energies for the processes are known (see below).

c. Gas-phase reactions of muonium. The study of the reactions of muonium in the gas phase is of considerable interest, since it permits a direct comparison with the gas-phase kinetics involving atomic hydrogen.

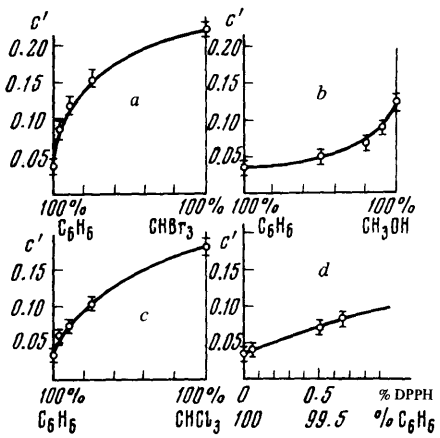


Figure 12. Variation of the asymmetry coefficients at the meson frequency with the concentration of the solution components (in mole %): *a*) $C_6H_6-CHBr_3$; *b*) $C_6H_6-CH_3OH$; *c*) $C_6H_6-CHCl_3$; *a*) C_6H_6–DPPH.

The presence of an inert buffer gas, which is necessary for the retardation of μ^+-mesons, permits the use of low concentrations of the test substance, i.e. a significant reduction of the rate of reaction, and the usual kinetic curves for the decrease in the amount of muonium with time at a given acceptor concentration may be studied. Calculation of the reaction rate constants is in this case trivial—the characteristic time of depolarisation (equivalent to the decrease of the concentration of muonium) is equal to the duration of the chemical reaction and is inversely proportional to the rate of reaction (V) with the acceptor at a concentration [Ac]:

$$\tau = \frac{1}{V} = \frac{1}{k\,[\mathrm{Ac}]} \quad . \qquad (5)$$

The calculations quoted below are based on the experimental data of Hughes and coworkers[94,95]. The inert buffer gas employed was carefully purified argon under a pressure of about 50 atm to which small admixtures of the test compounds (NO, O_2, NO_2, C_2H_4, H_2, N_2, etc.) were added. As an example, Fig. 13 presents the variation of the muonium depolarisation factor with time for various concentrations of ethylene at room temperature. The linear relation between the rate of depolarisation and the concentration of ethylene, which is evident from Fig. 13 (compare curves *1* and *2*), is evidence that the rate-limiting stage of the process is the formation of the radical $C_2H_4Mu^{\cdot}$, in which the depolarisation of the μ^+-meson takes place owing to the exchange interactions of the unpaired electron.

Standard kinetic treatment of the data in Fig. 13 leads to the characteristic times for the decrease of the polarisation of muonium (by a factor e) $\tau = (8.4 \pm 2.2) \times 10^{-6}$ s (curve *1*) and $\tau = (2.7_5 \pm 0.7) \times 10^{-6}$ s (curve *2*). The corresponding reaction rate constants $k = (1.7_5 \pm 0.4_5) \times 10^9$ litre mole^{-1} s^{-1} and $k = (1.4 \pm 0.4) \times 10^9$ litre mole^{-1} s^{-1} agree within the limits of experimental error. By combining the data, we have

$$K(\mathrm{Mu} + C_2H_4) = (1.6 \pm 0.3) \cdot 10^9 \text{ litre mole}^{-1}\,\text{s}^{-1}\,.$$

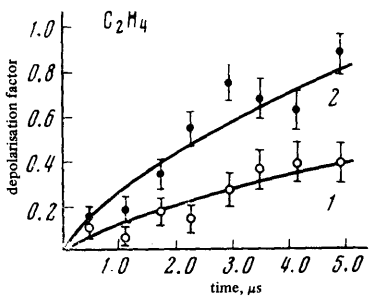


Figure 13. Kinetic curves for the decrease of polarisation (increase of the depolarisation factor) for muonium with time in the reaction with ethylene (according to Mobley et al.[94]): 1) $[C_2H_4] = 4.1 \times 10^{16}$ mol. cm^{-3}; 2) $[C_2H_4] = 15.8 \times 10^{16}$ mol. cm^{-3}.

The calculation for the analogous reaction of atomic hydrogen (according to collision theory, the rate constant ratio is about 3; in view of the low activation energies for the reactions of H and Mu with C_2H_4, it is not necessary to allow for the difference between them) yields the

$$k(\mathrm{H} + C_2H_4) = (5.3 \pm 1.0) \cdot 10^8 \text{ litre mole}^{-1}\,\text{s}^{-1},$$

in satisfactory agreement with the literature data[96,97] for the kinetics of the gas-phase reaction of H with C_2H_4 at 18°C, which gave

$$K(\mathrm{H} + C_2H_4) = (5.1 \div 7.5) \cdot 10^8 \text{ litre mole}^{-1}\,\text{s}^{-1}.$$

Experiments in longitudinal magnetic fields[95] showed that the strength of the critical magnetic field for NO and O_2 is consistent with the value of H_0 for the free muonium atom, confirming thereby the hypothesis of the dominant role of conversion processes in reactions with the given compounds. At the same time the critical field for C_2H_4 is significantly weaker (about 100 G), which is evidence of an increase of the effective distance between the meson and the unpaired electron as a result of the formation of the ethyl radical $C_2H_4Mu^{\cdot}$.

d. Temperature variation of the rates of the reactions of muonium. The activation energy for the process is one of the most important criteria of the reactivity of compounds. Having determined by the method described above the rate constants for the reactions at different temperatures, it is possible to obtain with an adequate statistical accuracy (which depends, in particular, on the width of the temperature range) the principal parameters of the chemical reactions of muonium

(the pre-exponential factor, the steric factor, and the activation energy).

Similar measurements have been made[98] for the substances listed in Table 3. Particular attention has been devoted to the phase transition point. For organic compounds, the continuous variation of the asymmetry coefficient during the change in the state of aggregation permitted the determination of the activation energies for the corresponding reactions of muonium. It is striking that, for the compounds investigated, the activation energies are low and do not exceed 1.5 kcal mole^{-1}. It is probably necessary to take into account the possible decrease of the activation energies for substitution reactions involving atoms with a smaller mass[99].

Table 3. Activation energies for the reactions of muonium.

Compound	Temp. range, °K	E, kcal mole^{-1}
C_6H_{12}	303÷77	1410±50
C_6H_5Br	303÷80	970±80
$CHBr_3$	303÷77	⩾670±50
H_2O (liq.)	363÷273	135±320
H_2O (solid)	273÷77	10±30

The abrupt change of the asymmetry coefficient for the water–ice phase transition (Fig. 14), corresponding to a decrease of the reaction rate constant by two powers of 10, is of interest. The interpretation of this effect must be related to the presence of hydrogen bonds in the crystal structure of ice[100]. When the temperature is reduced during the crystallisation of ice, a closed-coordination system of hydrogen bonds is formed, which gives rise to a sharp decrease of the rate of the process on transition to the crystal structure. In this case the free muonium atom in the ideal ice lattice migrates in the crystal owing to the impossibility of stabilisation by addition to hydrogen bonds. The evident conclusion is that muonium may be identified in ice, which has in fact been demonstrated[101]. The absence (within the limits of experimental error) of an activation barrier in the reaction of muonium with water and ice is also consistent with the specific nature of the process involving addition to the hydrogen bond.

The problem of barrier tunnelling interaction of muonium is of interest. Estimates based on a number of studies[33,94] showed that the temperature limit at which the rates of activation and tunnel processes become comparable may be reached at 30–70°K for muonium (for E = 1000–2000 cal mole^{-1} and an effective half-width of the activation barrier of 2–3 Å). Comparison with the analogous data for positronium, muonium, and atomic hydrogen will probably allow a solution of this theoretically important problem.

3. Reactions of Muonium with Unsaturated Compounds

a. Ratio of the rate constants for the formation of molecular and radical products. The interactions of muonium, like those of atomic hydrogen, with aromatic and other unsaturated compounds can occur, as already stated, by parallel pathways—substitution reactions with the removal of an atom and the formation of a diamagnetic molecule incorporating muonium and addition to a multiple bond with formation of a radical. The effect of the functional groups and substituents in the molecule and the role of factors involving the conjugation of different types of bonds were discovered in the study of the variation of the reaction rate constants associated with a successive logical alteration of molecular structure.

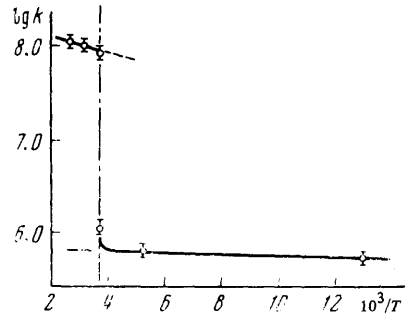


Figure 14. Temperature variation of the rate constant for the reaction of muonium with H_2O; the dot–dash line represents the temperature of the water–ice phase transition.

Table 4. Ratio of the rate constants for the reactions of muonium with methyl-substituted (in the ring) benzene derivatives.

Compound	k_2/k_1	$k_1\times10^{-9}$	$k_2\times10^{-9}$
C_6H_6	10.5±4.2	0.30±0.11	3.1±0.4
$C_6H_5CH_3$	3.3±1.0	0.77±0.20	2.5±0.7
$C_6H_4(CH_3)_2$	2.7±0.8	0.82±0.23	2.5±0.8
$C_6H_3(CH_3)_3$	2.3±0.6	1.03±0.22	2.4±0.7
$C_6H_2(CH_3)_4$	2.2±0.6	1.08±0.24	2.3±0.7
$C_6(CH_3)_6$	0.84±0.26	1.85±0.34	1.5±0.5

We shall examine, for example, the results[92] for two homologous series—for the successive methylation of the benzene ring and for the successive introduction of methyl groups into a side chain. In the first case (Fig. 15*a*) the polarisation increases relatively slightly up to the introduction of four methyl groups [as in durene (tetramethylbenzene)] but there is a subsequent increase of the asymmetry coefficient for hexamethylbenzene associated with the screening of the ring by CH_3 groups. These data indicate that the reaction involving the addition of muonium to the multiple bond predominates even under the conditions of partial screening of the benzene ring. It is significant that the polarisation for hexamethylbenzene is nevertheless appreciably less than for saturated compounds (octane and cyclohexane). One may suppose that this difference is caused by the attack of muonium in the plane of the benzene ring with formation of a π-complex. Quantitative calculation yields the reaction rate constants (litre mole^{-1} s^{-1}) listed in Table 4.

We may note that the overall reaction rate constants hardly change in this series, but there is a redistribution of the reactivity of the molecule with respect to parallel reaction pathways.

The analogous relations for normal (unbranched) alkylbenzenes are of a different type (Fig. 15*b* and Table 5). With increase of the length of the side chain, there is a monotonic increase of the asymmetry coefficient and an equivalent increase of the rate constant for the formation of molecular products. This change corresponds to the absence of a redistribution among parallel reaction pathways. This result is of very general importance, since it indicates the independence of the interactions of muonium with aromatic rings and the side chains when the chain length is sufficiently long (more than two carbon atoms).

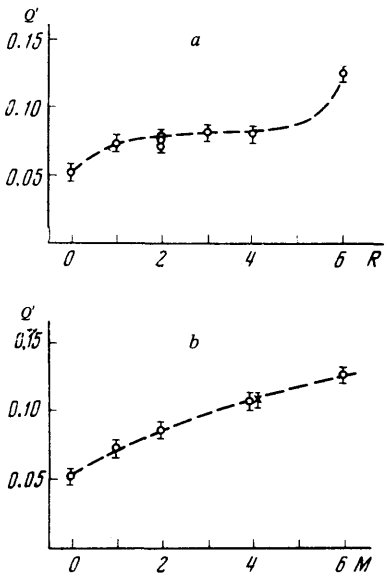


Figure 15. Variation of the asymmetry coefficient with the number of methyl groups R in the benzene ring (*a*) and with the number of carbon atoms (M) in the side chain of n-alkylbenzenes (*b*); X = $C_6H_5CH(C_2H_5)C_3H_7$.

The hypothesis that in many cases the interaction does not take place with the molecule as a whole but with individual fragments is confirmed by the experiment with 3-phenylhexane for which the reaction rate constants agree for the analogous values for n-butylbenzene (Table 5).

Many other results confirming the probable future value of this research technique for the investigation of the relation between the reactivity of the molecule and its chemical structure are quoted in the literature[92,93,102].

b. The restoration of polarisation in longitudinal magnetic fields. The effect of external magnetic fields on the polarisation of the μe decomposition when muonium interacts with unsaturated compounds revealed the presence[103-105] of as a rule two polarisation components. The first component, which is independent of the strength of the transverse magnetic field, is due to a substitution reaction with formation of diamagnetic molecular products containing muonium. The second component depends on the longitudinal magnetic field; however, both the initial (at $H \simeq 0$) polarisation and the critical magnetic field strength are not consistent with the hypothesis of a simple Paschen–Back effect associated with the prevention of depolarisation owing to the uncoupling of the magnetic moments of the μ^+-meson and the electron in a free (isolated) muonium atom.

Table 5. Ratio of the rate constants for the reactions of muonium with alkylbenzenes.

Compound	$(k_1+k_2)\times10^{-9}$	k_2/k_1	$k_1\times10^{-9}$
C_6H_6	3.4±0.3	10.5±4.2	0.30±0.11
$C_6H_5CH_3$	3.3±0.4	3.3±1.0	0.77±0.20
$C_6H_5C_2H_5$	3.6±0.8	2.4±0.8	1.05±0.30
$C_6H_5C_4H_9$	4.3±0.9	1.4±0.3	1.8±0.6
$C_6H_5C_6H_{13}$	5.7±1.0	0.78±0.22	3.2±0.7
$C_6H_5CH(C_2H_5)C_3H_7$	4.3±0.9	1.4±0.3	1.8±0.6

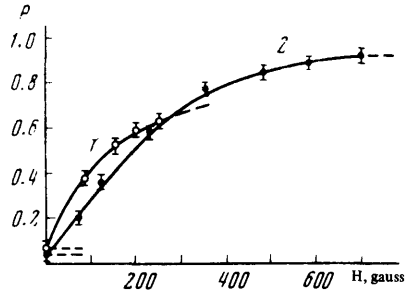


Figure 16. Variation of polarisation with longitudinal magnetic field strength. The lower dashed lines correspond to polarisation in a transverse magnetic field: 1) benzene; 2) naphthalene.

In these cases when a muonium atom adds to a multiple bond forming a radical with an unpaired electron, a complex system of spin interactions of the magnetic moments of the delocalised (in the general case) electron, the μ^+- meson, and the adjacent nuclei (protons) in the molecule is achieved and leads to depolarisation. The latter is removed when the strength of the longitudinal magnetic field corresponds to a change in the average effective distance between the meson and the delocalised electron in the molecule, the limiting asymptotic value of the polarisation corresponding to the overall rate of interaction via the molecular (component independence of the transverse magnetic field strength) and radical reaction pathways.

We shall consider as an example the results obtained[106] for the restoration of polarisation in crystalline benzene (−196°C) and naphthalene (30°C) specimens. The reason for the use of a solid phase is that molecular rotation during the period of observation may lead to an averaging of the interactions of the magnetic moments[87]. If the moment of inertia of the molecule is sufficiently high, the rotation during a period of the order of the lifetime of the μ^+-meson can be of course neglected. Fig. 16 shows that the polarisation is restored along curves with different parameters and there are differences between both the asymptotic limits to which the polarisation tends with increasing field strength and between the critical magnetic field strengths. Using the overall values for the reactivity

of benzene obtained by the method of competing acceptors, we find that at $-196°C$, $P = 0.79 \pm 0.03$, which is in satisfactory agreement with the asymptotic limit (Fig. 16). The estimates based on the difference between the reactivities of benzene and naphthalene in reactions involving addition to a multiple bond[86,106] show that, within the limits of the accuracy of the measurements, the asymptotic polarisation limit for naphthalene should be unity, in agreement with experimental data.

The difference between the critical magnetic field strengths (86 ± 6 G for benzene and 168 ± 11 G for naphthalene) is qualitatively consistent with the hypothesis concerning the effect of quaternary carbon atoms on the distribution of the probability density of the unpaired electron in the $C_{10}H_8Mu^{\cdot}$ radical. Quantitative analysis of the results requires detailed quantum-chemical calculations. Adopting the very rough approximation that the nature of the interaction of the magnetic moments of the μ^+-meson and the electron in the radical is the same as in the muonium atom and depends only on the average effective distance (r_{eff}), we obtain $r_{eff} = 1.40 \pm 0.03$ Å for benzene and $r_{eff} = 1.12 \pm 0.02$ Å for naphthalene. Without carrying out a specific physical interpretation of these values, we shall only point out the high experimental (but not computational) accuracy of the determination of r_{eff}.

4. Other Types of Interaction of Muonium

Like atomic hydrogen, the free muonium atom can also enter into redox reactions with variable-valence ions involving electron transfer (for example, $Mu + Fe^{3+} \rightarrow \mu^+ + Fe^{2+}$). However, these reactions are less specific for muonium, since, firstly, the indeterminacy of the further behaviour of the meson (or of the system in which it is incorporated) remains, secondly, the interaction with a solvent, which is inevitably present, becomes important, and, thirdly, the role of conversion exchange is much more pronounced for paramagnetic species.

Certain experiments on Cu^{2+}, Fe^{2+}, and Fe^{3+} ions[93] showed that the accuracy of the determination of the rate constants for the reactions of muonium in these cases is low and there is only a qualitative correspondence with the analogous reactions of atomic hydrogen investigated in the radiation chemistry of aqueous solutions[107]. The study of redox reactions with ions in solution is most promising for processes involving positronium, since there is for the latter a specific relation between the lifetime and the change in electronic state.

Conversion exchange is most important for compounds with unpaired electrons (NO, O_2, etc.). Despite the high rates of chemical reactions with these compounds, conversion exchange involving them predominates and the cross-sections for the processes are close to the gas-kinetic collision factors[94].

Interesting possibilities arise in the study of diamagnetic molecules incorporating muonium under conditions where there is a relation between the magnetic moments of the μ^+-meson and of an adjacent nucleus. Precession in a magnetic field which is not strong enough to uncouple the magnetic moments of the meson and the nucleus should be determined by the overall magnetic moment and the spin of the system. In particular, as a result of the vector addition of the magnetic moments and the spins of the proton and meson, the precession frequency in the transverse field for certain states of the MuH molecule should be 0.343 and the asymmetry coefficient should be half of the corresponding value for the precession of the μ^+-meson incorporated in the molecule. This constitutes the basis of one of the possible ways of identifying individual products[91] formed in the reactions of muonium with matter.

Among other aspects of the application of the μ^+-meson and muonium, we may mention the study of their interactions with a crystal lattice, which is of interest for the physics of solids and semiconductors. The slow (of the order of several microseconds) depolarisation effect during the time of observation found for a number of substances (B_4C, LiH, etc.[90,108]) is significant in the study of the spin–lattice relaxation of a polarised ion, of crystal structures, and of the role of local magnetic fields. In semiconductors[109,110] the introduction of alloying additives and also a change of temperature revealed a complete spectrum of polarisation changes as a function of the concentration of charge carriers in the specimen. Identification of the precession of triplet muonium in germanium single crystals at 77°K demonstrated[110] a low contribution by the exchange interaction with the electrons of the medium under the given conditions. The role of possible conversion exchange processes involving the lattice anions has been elucidated for the single crystals of a number of alkali metal halides[111,112]. The study of crystal lattice defects demonstrated that the latter are appreciable but do not alter the overall nature of the observed phenomena.

IV. MESONIC ATOMS

A number of very interesting effects are observed in the study of the effect of chemical structure on the atomic capture of μ^-- and π^--mesons in various substances. Negatively charged mesons retarded in a given medium are ultimately captured by atomic orbitals forming mesonic atoms in which they play the role of "heavy electrons". Initially the capture takes place usually in orbitals with high quantum numbers ($n = 10-15$) and then, as a result of a series of cascade transitions with emission of mesonic X-rays, the meson reaches the ground energy state in the inner $K(1s)$ shell of the given atom. As already stated, the radii of a mesonic atom orbital are close to nuclear dimensions and the atom of mesohydrogen, for example, behaves as a single electrically neutral particle. It can approach various nuclei and interact with them without the interference normally caused by the electrostatic repulsion between the nucleus and the proton. In particular mesonic hydrogen can behave as a kind of catalyst of the cold mesonuclear synthesis of helium from hydrogen[113].

In the capture of a μ^--meson, there arises both a characteristic mesonic X-ray emission spectrum and the lifetime of the μ^--meson in the 1s shell changes as a function of the atomic number z of the nucleus. By studying these factors in various compounds, it was possible to establish the probability of the atomic capture of μ^--mesons by individual components.

Theoretical hypotheses concerning the additivity of capture in a multicomponent system give rise to the expression (the Fermi–Teller z law)

$$W_i = \frac{n_i z_i}{\Sigma n_i z_i} \quad ,$$

where W is the probability of the capture of the μ^--meson, n the concentration of the atoms of the ith component, and z the atomic number. Numerous experiments showed that this relation does not constitute the rule but is a rare exception—it holds satisfactorily only for metallic alloys.

A detailed study[114] of the probabilities of the atomic capture of μ^--mesons in a number of oxides ($z = 4-82$) led to the conclusion that the ratio of the capture probabilities per nucleus of the given element $[W(z)]_\mu$ and oxygen $[W(0)]_\mu$ varies periodically. The experimental relation $[W(z)/W(0)]_\mu = f(z)$ is plotted in Fig. 17.

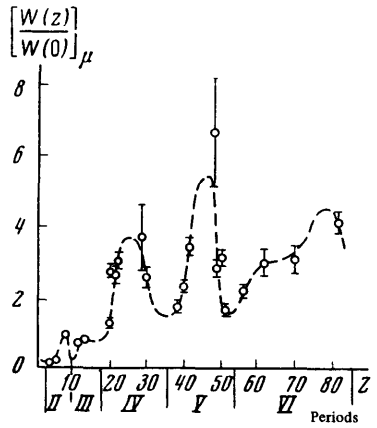


Figure 17. The ratio of the probabilities of the atomic capture of μ^--mesons in oxides. $W(z)$ and $W(0)$—probabilities of meson capture per nucleus z and per oxygen nucleus respectively.

Such periodicity is quite unexpected in terms of the concepts concerning the capture of mesons directly by atomic orbitals. However, it can be satisfactorily explained within the framework of the "model of large mesonic molecules"[115], according to which the mesons are initially captured by generalised mesonic molecular levels, the quantum numbers of which are so large that they correspond to the usual atomic dimensions (about 10^{-8} cm), despite the fact that the linear scale of mesonic atoms is smaller by a factor of 200 compared with the usual atoms. Thus the μ^--meson is located in an asymmetric double potential well (Fig. 18). The probability of the transfer of the meson to lower levels of one or other atom in cascade transitions to the region where the mesonic levels of the two atoms are separated depends on the properties of the electron shells of both. Clearly the periodicity of the structure of the outer shells of one of the atoms while that of the other remains unchanged (in the given case of oxides, this is oxygen) may lead to the appearance of a periodic variation of the probability ratio $[W(z)/W(0)]_\mu$.

The ratios of the probability of the capture of μ^--mesons by atomic orbitals are equivalent to the ratio of the effective atomic dimensions in complicated compounds. Thus there is a possibility of investigating the distribution of electron density in molecules, i.e. of a quantitative experimental determination of the amount of ionic character (covalence) of chemical bonds in polyatomic compounds.

The model of large mesonic molecules has been applied also to relations governing the capture of slow π^--mesons in mixtures and in chemical compounds involving hydrogen. In hydrogen such capture is accompanied by a charge-transfer reaction:

$$\pi^- + p \rightarrow \pi^0 + n$$

(the capture takes place partly according to the mechanism $\pi^- + p \rightarrow \gamma + n$) and the resulting slow π^0-meson decomposes after about 10^{-16} s into two γ-quanta moving apart at an angle of 180°C. In the capture of π^--mesons in complex nuclei, there is no charge transfer or the second process indicated above; in this case the capture of π^--mesons is accompanied by the ejection of numerous nucleons ("star"). Therefore the determination of the yield of π^--mesons, for example, by recording the coincidences due to the 2γ-quanta, constitutes a reliable criterion for the determination of the fraction of π^--mesons captured in complex systems by hydrogen atoms.

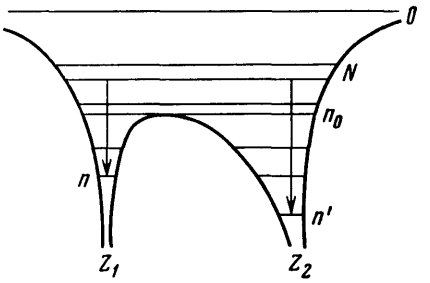


Figure 18. Schematic representation of the meson levels in an asymmetric diatomic molecule z_1z_2. The levels above n_0 are common mesomolecular levels; the mesonic atomic levels z_1 and z_2 are shown below.

It has been shown in a series of studies[116-118] that the ratio of the probabilities of the capture of slow π^--mesons by protons and nuclei with a charge Z differs sharply for simple mixtures and chemical compounds (Z and H). Whereas for $Z_m + (H_2)_n$ mixtures the ratio is $[W(H)/W(Z)]_\pi \simeq 2n/mz$, in binary compounds of analogous composition the ratio is smaller by a factor Z^2. For example in the $N_2 + 2H_2$ gas mixture the probability of the capture of π^--mesons by hydrogen is 30%, while in hydrazine (N_2H_4) the probability is reduced almost to 1/200. The finding that $[W(H)/W(Z)]_\pi$ depends on the nature of the chemical bond is even more interesting. Thus for ethylene (C_2H_4) $[W(H)/W(Z)]_\pi$ is higher than for acetylene (C_2H_2) by a factor of 2.5 and not 2. Thus fine differences between the $H_2C{=}CH{-}H$ and $HC{-}C{\equiv}H$ bonds are shown in the capture of π^--mesons, and are probably reflected in a slightly higher C–H bond energy in acetylene compared with ethylene.

We may note that the method applied provides a sensitive criterion for the determination of the difference between hydrogen involved in exchange interactions (in the molecule) and free hydrogen[119], which is very useful for the elucidation of many problems in structural chemistry, kinetics, and catalysis of chemical reactions. In particular, such problems may include the kinetics and catalysis of reactions of the type $Z + H_2 \rightarrow Z_mH_n$, the nature and kinetics of adsorption, sorption, and chemisorption phenomena, the role of water of crystallisation in compounds, the structure of ice at low temperatures, and the nature of hydrogen bonds.

As an illustration, one may point to the lower probability of the capture of π^--mesons by hydrogen in titanium hydrides[120] compared with the theoretical values, which is

probably due to the characteristics of the hydrogen bond in pseudohydrides. Although the nature of the hydrogen bond with the metal in compounds of this kind has not been finally elucidated, it has been suggested that in pseudohydrides the hydrogen is partly involved in chemical interactions and partly ionised and exists in the form of a proton gas[121]. Since only chemically combined hydrogen is involved in the capture of π^--mesons, it is reasonable to expect a lower probability of their capture in pseudohydrides compared with the usual hydrogen-containing compounds. Thus the result obtained confirms the above hypothesis: it is also possible to estimate the fraction of ionised hydrogen (protons) in pseudohydrides. Experiments on the problem of the spatial and temporal delocalisation (this problem has been considered theoretically by Blyumenfel'd et al.[122]) of π^--mesons among systems comprising several identical ZH groups in symmetrical compounds of the type $R(ZH)_q$,[120] and also on the problems of the determination of the amounts of ionic character of O–H bonds in various oxygen-containing acids, are being carried out. A number of interesting data concerning the intensity ratio of π^--mesonic X-ray emission lines associated with changes in chemical structure have been obtained[123].

At the present time both the development of theoretical concepts and of the techniques of mesochemical experiments are far from complete. Nevertheless, comparison of the experimental probabilities of meson capture with theoretical estimates already yields very interesting data. So far, experiments with μ^-- and π^-- mesonic atoms reduce as a rule to the study of the effect of the known properties of various compounds on the catpure characteristics. The converse problem now arises in nuclear chemistry—the employment of the properties of mesoatomic systems to obtain hitherto unknown characteristics of chemical bonds, i.e. the problem of creating mesochemical research methods.

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The scope of studies with the aid of elementary particles constitutes, as a whole, a novel set of nuclear-physical methods which may prove suitable for the solution of many physicochemical problems. The principal aim of this review was to outline the range of problems where these methods yield information of interest for chemical research. Undoubtedly further expansion of studies in this field will reveal other important aspects of the application of the chemistry of new atoms.

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The Heterogeneity of Natural Lignin

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The results of investigations of the molecular-weight distribution of lignin in the delignification of wood by various methods, modern ideas on the distribution of lignin in cell walls of plant tissues, and the presence of bonding between the lignin and the carbohydrate components are critically examined. The results obtained in the course of these investigations show that natural lignin evidently consists of two main components which differ in molecular weight, in their localisation in the cell walls of the plant tissues, in the nature and number of the bonds with the carbohydrate components of the wood, and also in the topochemical models at the time of delignification.
The present review is the first attempt to survey the results relating to the problem of the heterogeneity of natural lignin. There is a bibliography of 143 references.

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I. INTRODUCTION

The problem of the homogeneity or heterogeneity of natural (that is, not isolated from plant tissue) lignin is of both theoretical and practical interest. The establishment of homogeneity or heterogeneity of natural lignin is undoubtedly a necessary prerequisite for solving the problem of the nature and number of lignocarbohydrate bonds in plant tissues. As is well known, this problem is of considerable interest and is now attracting the attention of investigators both in the USSR and abroad. Furthermore, the importance of information about the homogeneity or heterogeneity of lignin is also apparent in the development of rational industrial processes for the delignification of vegetable raw materials.

At the same time the complexity of the solution of this problem is primarily due to the fact that wood chemistry does not yet have a method for isolating lignin from lignified plant tissues which does not involve the use of acids, alkalis, or mechanical action, which change natural lignin to a greater or lesser extent. However, despite this the intensive development of the physical chemistry of lignin which began in the middle of the 1950s and was linked with progress in the physical chemistry of polymers which had benefitted by a series of promising methods of investigation, led to the obtaining of a considerable number of results relating to this problem. These results concerned the mechanisms observable in the isolation of lignin from wood by various methods, the distribution of lignin in the cell walls of plant tissues, the nature of the bonds between lignin and carbohydrate constituents and various other questions. The generalisation of these results allows a representation of the present state of the problem of the heterogeneity of natural lignin to be compiled.

In conclusion we note that the results examined in the present review mainly relate to the lignin of coniferous species, which have been investigated most.

II. MOLECULAR WEIGHTS OF PREPARATIONS OF LIGNIN ISOLATED AT SUCCESSIVE STAGES OF THE DELIGNIFICATION OF WOOD

The results of the investigations [1-12] on the fractionation of lignosulphonates isolated as a result of the sulphite digestion of wood, made in the 1940s and 1950s, showed that these preparations had a considerable polydispersity. McCarthy and coworkers [13] made the first attempt to connect the change in molecular weight of the lignosulphonates isolated with the degree of delignification of the wood. They subjected wood flour from *Tsuga*, spruce, and maple to treatment with $NaHSO_3$–H_2SO_3 solutions at 135°C for various intervals of time. It was found that for coniferous woods (*Tsuga* and spruce) the molecular weights of the soluble lignosulphonates isolated as a result of brief (30 min) digestions amount to ~ 2000–4000 (diffusion method). On increasing the duration of the digestion the molecular weight of the lignosulphonates increases as the delignification of the wood proceeds, reaching the maximal value of ~ 11 000 at almost complete delignification (4 to 5 h digestion). Longer digestion reduced the molecular weight to a minimal value of ~ 5000 and, for *Tsuga*, then led to a further increase. The investigators associated these maximal and minimal values of the molecular weights of the lignosulphonates with the action of three processes which occur simultaneously during the sulphite digestion but at different rates: (a) the hydrolysis of hydrolysable bonds in the polymeric lignin; (b) the differential diffusion of soluble lignosulphonates from the wood tissue, with the finer fragments diffusing first; and (c) the irreversible autocondensation of the macromolecules of the lignosulphonates.

A serious drawback of the method used by these investigators is that the dissolution of the lignin is cumulative, so that each fraction contains not only the material dissolved during the given interval of the treatment but also products from the degradation of the lignosulphonates

which had been transferred to the solution in earlier stages of the digestion. The interpretation of these results is hindered by the fact that the main heterogeneous reaction is accompanied by a homogeneous reaction in which the lignosulphonate that has already dissolved undergoes various chemical changes.

Felicetta and McCarthy [14] attempted to improve the cumulative method considered above by "incremental" delignification, in which the wood is treated with the digestion solution in several successive stages. After each stage the residue is separated and subjected to further treatment. They delignified *Tsuga* wood by five successive treatments with $NaHSO_3$–H_2SO_3 solutions, each of which was continued for ~15 h at 130°C. An increased dissolution of the lignin was brought about by increasing the concentration of free SO_2 after each stage except the first (pH of digestion: 4.8, 4.8, 3.4, 2.5, and 2.1). The molecular weights of the lignosulphonates increased from 3400 to 30 000 (diffusion method) in the first four digestions. The final sulphite treatment led to the isolation of a lignosulphonate with molecular weight 20500.

Table 1. Characteristics of the fractions of dioxan-lignin isolated as a result of four successive extractions of spruce wood [15].

Fraction	Yield, % of Klason lignin		Contents, %		M_w	D_A, $cm^2 s^{-1}$	E_{280}, litre $cm^{-1} g^{-1}$	dn/dc, $ml\ g^{-1}$	$\bar{v}$, $ml\ g^{-1}$
	not purified	purified	OCH_3	carbohydrates					
1	18.1	12.7	15.4	0.03	4300	$1.77 \cdot 10^{-6}$	19.8	0.113	0.703
2	25.0	17.0	15.5	0.02	7400	$1.22 \cdot 10^{-6}$	20.8	0.116	0.712
3	21.0	16.2	15.9	0.03	33000	$0.775 \cdot 10^{-6}$	22.1	0.124	0.693
4	17.6	12.9	15.5	0.03	85000	$0.55 \cdot 10^{-6}$	23.3	0.135	0.701

Rezanowich and coworkers [15] observed a similar tendency to an increase in the molecular weight of the lignin preparations with progress in the delignification of wood during four successive extractions of white spruce sawdust with aqueous dioxan containing a little hydrochloric acid, by Pepper's method [16]. The dioxan-lignin fractions obtained contained methoxyl groups and carbohydrate impurities which showed ultraviolet absorption at 280 mμm (E_{280}), an increase in the refractive index increment (dn/dc), characteristic viscosity, diffusion constant (D_A), partial specific volume ($\bar{v}$), and molecular weight (M_w), determined by sedimentation equilibrium in an ultracentrifuge (Table 1). These results show the homogeneity of the dioxan-lignin fractions in respect of the content of methoxyl groups and carbohydrate impurities, and also of the partial specific volumes. Nevertheless, with increase in the molecular weight of the fractions there is a small but definite increase in the ultraviolet light absorption and in dn/dc. Rezanowich and coworkers [15] consider that these changes in dn/dc and E_{280} are probably connected with differences in the chemical structure of the fractions, and these in turn may be due to the heterogeneity of the lignin in the wood. For example, the dioxan-lignin fractions which are extracted later can contain a greater proportion of biphenyl bonds which could explain the higher molecular weights and refractive index increment observable for these preparations. On the other hand, the chemical changes which accompany the changes in dn/dc and E_{280} can be the result of the prolonged acidolysis of the last fractions, which can also lead to an increase in their molecular weight, owing to polymerisation. Although their results cannot be interpreted with certainty, the investigators assume that slight structural heterogeneity of the dioxan-lignins extractible from spruce wood is superimposed on their polydispersity over a wide range of molecular weights.

Yean and coworkers [17] isolated five lignosulphonate fractions as a result of the successive extraction of spruce wood flour with an acid sulphite solution. The weight-mean molecular weights of the resulting preparations, determined by sedimentation equilibrium in the ultracentrifuge and by light scattering, ranged from 5000 to 130000, increasing with quantity of lignin extracted from the wood. The ratio M_w/M_n, calculated on the basis of the weight distribution, was 3.1, which shows the appreciable polydispersity of the lignosulphonates isolated in sulphite digestion of spruce wood. This polydispersity is confirmed by the experimental separation of one of the fractions with molecular weight 95 200 by dialysis through membranes with successively increasing pore dimensions as a result of which nine subfractions with molecular weights from 37 000 to 1 270 000 were obtained.

Arlt and Schuerch [18] investigated four fractions of ethanol-lignin, isolated by successive extraction of spruce wood with 0.2 *N* HCl (gas) in an anhydrous mixture (4 : 1) of chloroform and ethanol at 60°C according to a method developed earlier [19]. Table 2 gives some results from this investigation; they relate to ether-insoluble fractions of the ethanol-lignin which had dissolved in chloroform, after their purification from carbohydrates.

Table 2. Characteristics of the fractions of ethanol-lignin isolated as a result of four successive extractions of spruce wood [18].

Fraction	Yield, % of Klason lignin*	Contents, %					Molecular weight (cryoscopic, in ethylene carbonate
		C	H	OCH_3	OC_2H_5	OH_{phen}	
1	33.3	61.24	6.66	12.7	10.00	2.88	528
2	18.4	62.44	6.62	14.3	8.28	2.86	729
3	9.9	62.96	6.34	14.8	6.97	2.72	827
4	8.9	60.74	6.02	14.8	7.55	3.23	1070

*Calculated by us from published results [18,19].

Successive treatments of lignified material with a mixture (1 : 4) of nitric acid (specific gravity 1.4) and 96% ethanol at the boiling point was proposed by Kürschner and Hoffer [20,21] as a method for the delignification of wood. On the basis of the results of an analytical investigation of the fractions obtained by the fractional precipitation of nitrolignin from the combined reaction solutions after several successive digestions of a single portion of spruce wood, Kürschner [22] concluded that the nitrolignin isolated in alcoholic nitration is a homogeneous product. This conclusion met with objections from Fuchs [23], who, by starting from the premise of the heterogeneity of the lignin in the wood, assumed that it could not be homogeneous in its derivative, nitrolignin. On the basis of the results of a chromatographic examination of the nitrolignin isolated from the combined reaction solutions after several successive digestions of a single portion of spruce wood under the conditions of the Kürschner method,

Chuksanova and coworkers[24] concluded that it was heterogeneous: the fractions obtained differed significantly in molecular weight. A more detailed investigation, made by Grushnikov and Shorygina[25], showed that the nitrolignins isolated after each of the successive digestions of spruce wood under the conditions of this method are similar as regards both elemental analyses and functional groups, and also spectroscopically. Nevertheless the molecular weight of nitrolignin isolated after the first nitration is about half that of the nitrolignins isolated after subsequent digestions[26]. Table 3 gives some of the results of this investigation.

Table 3. Characteristics of nitrolignins isolated as a result of successive nitric acid digestions of spruce wood[25,26].

Nitrolignin isolated after nitration	Yield, % of Komarov lignin	Contents, %		Contents, moles per C_6–C_3				Molecular weight (ebullioscopic, in absolute dioxan)
		C	H	NO_2	OCH_3	OC_2H_5	O_2 (COOH)	
First series of experiments								
1	21.0	51.88	5.14	0.79	0.88	0.27	0.25	1524
2	17.2	51.32	5.05	0.73	0.94	0.20	0.28	3054
3	12.0	51.92	4.82	0.74	0.86	0.19	0.29	3105
4	8.2	51.92	4.78	0.74	0.88	0.22	0.27	—
Second series of experiments								
1	26.3	51.26	5.00	0.66	0.92	0.17	0.30	1596
2	17.3	50.20	4.96	0.80	0.94	0.12	0.31	2783
3	10.9	50.38	5.07	0.68	0.89	0.20	0.32	3190
4	5.5	50.17	4.95	0.74	0.92	0.16	0.26	—

Each of the above methods of wood delignification suffers from a significant drawback, the possibility of irreversible changes occurring in the undissolved lignin during the repeated operations of filtration and washing needed to separate the residue from the digestion solutions. A special hazard is the sorption of molecular oxygen, which in repeat heating can facilitate an increase in the molecular weight of the preparations isolated, due to the polymerisation of the lignin.

These drawbacks are eliminated in continuous digestion, in which the wood is treated in a specially constructed autoclave in a continuous stream of digestion liquid at the temperature and pressure corresponding to the standard digestion conditions. Continuous digestion allows the dissolved material to be constantly removed from the autoclave without being subjected to the further action of the digestion solution and it also ensures the absence of contact between the wood being digested and the atmosphere, thus eliminating the possibility of secondary changes in the lignin.

Yean and Goring[27] undertook the acid sulphite digestion (135°C; total SO_2 concentration ~6%) of spruce sawdust by a continuous process. Six specimens of digestion liquid, representing the soluble material at successive stages of the wood delignification process, were withdrawn. The lignosulphonates isolated from these specimens were freed from low-molecular-weight impurities by dialysis and from non-dialysable polysaccharides by electrophoresis-convection. The purified lignosulphonates were analogous in the contents of sulphur and methoxy-groups and also in ultraviolet light absorption (E_{280}) and refractive index increment (dn/dc) (Table 4). However, the mean molecular weight (M_w) increased from 9700 to 143 000 (sedimentation equilibrium in an ultracentrifuge) as the wood was delignified. To investigate the possibility of the condensation of the lignin during treatment with acid hydrogen sulphite solution, two of the fractions isolated were subjected to repeat digestions under various conditions. In every instance degradation of the lignin was observed†. These results were thought by Yean and Goring to show that in acid sulphite digestion polymerisation of lignin either does not occur or is completed in the early stages of the digestion.

Table 4. Characteristics of the fractions of lignosulphonate isolated at various stages of acid sulphite digestion[27].

Fraction	Degree of delignification, %	Contents, %		M_w	E_{280}, litre $cm^{-1} g^{-1}$	dn/ds, ml g^{-1}
		OCH_3	S			
1	13.3	13.6	4.7	9700	12.1	0.189
2	34.2	13.4	4.8	22 900	12.4	0.191
3	49.7	12.5	4.4	39 000	12.6	0.181
4	65.1	14.0	4.7	75 400	12.9	0.192
5	79.0	13.8	4.9	100 000	13.2	0.197
6	92.5	14.0	5.7	143 000	13.9	0.198

The results of these investigations showed that ~40% of the lignosulphonate isolated from spruce wood as a result of acid sulphite digestion is capable of being dialysed and consequently has a molecular weight of < 5000. The remaining 60% has a molecular weight in the range from 9700 to 143 000. This molecular weight distribution enabled the investigators to postulate the existence of two types of lignin in spruce wood: low- and high-molecular-weight types and it was suggested that they were localised in different parts of the cell wall of the fibre. To check this assumption Yean and Goring[29] investigated lignosulphonates isolated from morphologically different parts of the wood structure. The differencs between sapwood and heartwood, earlywood and latewood, compressionwood, tensionwood, and ordinary wood were investigated. However, no significant differences in molecular weight were observed between the lignosulphonates isolated on the basis of which it could be concluded that the wide range of molecular weights observed earlier was unconnected with the morphological differences investigated. It was assumed that the results obtained could be explained on in molecular weight of the lignins localised in the material of the middle plate and in the secondary wall, or on the basis of the assumption that in the parts of the wood structure investigated lignins with different molecular weights are homogeneously mixed at the molecular level.

Yean and Goring[30] made a hydrogen sulphite digestion (153°C, pH 4) of spruce wood sawdust by a continuous process. Four specimens with approximately the same weight percentage of lignin were withdrawn during the digestion. The lignosulphonates isolated were purified by dialysis and moving boundary electrophoresis and were then analogous in the contents of methoxyl groups

†According to Reznikov's results[28] even relatively mild chemical action (acid treatment at ⩾ 100°C) of both the lignins isolated and the lignin in wood leads to the condensation of the macromolecules in the solid phase. In this connection Reznikov assumes that from the results on the molecular weights of preparations of lignin isolated from acid medium it is impossible to obtain even approximate ideas of the molecular weight of the lignin in the wood.

and sulphur, ultraviolet absorption (E_{280}), refractive index increment (dn/dc), and also infrared spectra (Table 5). Simultaneously the weighed mean molecular weight (M_w) increased from 10 000 (sedimentation equilibrium in an ultracentrifuge) for the first fraction to 77 000 for the final fraction.

Table 5. Characteristics of the fractions of lignosulphonate isolated at various stages of the hydrogen sulphite digestion of spruce wood[30].

Fraction	Degree of delignification, %	Contents, %		M_w	E_{280}, litre $cm^{-1}\,g^{-1}$	dn/dc, ml g^{-1}
		OCH_3	S			
1	8.3	11.8	6.2	10 000	13.3	0.185
2	26.6	12.8	5.6	13 600	12.1	0.181
3	43.1	12.9	5.2	31 000	12.8	0.191
4	54.9	12.6	5.5	77 000	14.1	0.198

A similar tendency for an increase in the molecular weights of lignin fractions during the course of the delignification of wood was also observed in continuous kraft digestion[31]. Some results are given in Table 6.

Table 6. Characteristics of the fraction of kraft lignin isolated at different stages of the kraft digestion of spruce wood[31].

Fraction	Degree of delignification, %	Contents, %			M_w	E_{280}, litre $cm^{-1}\,g^{-1}$	dn/dc, ml g^{-1}
		carbohydrates	OCH_3	S			
1	5.5	22	12.1	2.5	1780	20.5	0.191
2	17.2	9	11.2	2.1	11 700	18.8	0.188
3	31.0	16	12.5	1.7	13 100	18.4	0.211
4	45.0	11	12.2	1.5	15 500	18.5	0.211
5	60.0	14	13.1	2.1	32 800	19.0	0.190
6	75.0	12	12.5	1.5	30 900	18.8	0.201
7	88.0	3	11.8	1.7	51 000	17.2	0.197

As the results show, seven fractions representing different stages of the delignification of spruce wood had analogous methoxy-group contents, ultraviolet absorption (E_{280}), and refractive index increment (dn/dc), but their weight mean molecular weights (M_w) increased from 1800 (sedimentation equilibrium in an ultracentrifuge) for the first fraction to 51 000 for the final fraction. Gel filtration on Sephadexes showed the considerable polydispersity of the fractions isolated.

The authors consider that the above results for acid sulphite[27], hydrogen sulphite[30], and kraft[31] digestions of spruce wood by continuous processes have shown that the different processes used for the dissolution of wood lignin do not alter its structural properties to any great extent, as is shown by the similarity in orders of magnitude of the methoxy-group content, ultraviolet absorption, and refractive index increment for lignosulphonates obtained as a result of acid sulphite and hydrogen sulphite digestions and also for kraft lignins (Table 7). In a comparison of lignosulphonates isolated as a result of the acid sulphite and hydrogen sulphite digestions their similar molecular weights at similar degrees of delignification of the wood is noteworthy. In comparison with the lignosulphonates, the kraft lignins have a lower molecular weight than the lignosulphonates, which is attributed to the more rapid degradation of the lignin in the kraft digestion. This regularity can be readily observed in Fig. 1, which shows the change in the molecular weight of the lignin preparations isolated during the course of the wood delignification.

Table 7. Mean value of the content of OCH_3 groups, absorption of ultraviolet light (E_{280}), and refractive index increment (dn/dc) for lignin derivatives isolated as a result of three different digestion processes.

Process	Content of OCH_3 groups, %	E_{280}, litre $cm^{-1}\,g^{-1}$	dn/dc, ml g^{-1}
Acid sulphite (Ref.27)	13.6 (±0.4)	12.8 (±0.5)	0.191 (±0.004)
Hydrogen sulphite (Ref.30)	12.5 (±0.4)	13.1 (±0.6)	0.189 (±0.006)
Kraft (Ref.31)	12.2 (±0.4)	18.7 (±1.6)	0.198 (±0.008)

Brown and coworkers[32,33] investigated the isolation of lignin from liquidambar and spruce woods with the aid of brown rot fungus. Lignin preparations were obtained by extracting the wood with dimethylformamide at successive stages of increased enzymatic removal of carbohydrates: 10.5, 27.1, 47.1, 59.5, 77.2, 80.5, 92.6, 97.7, and 100%.

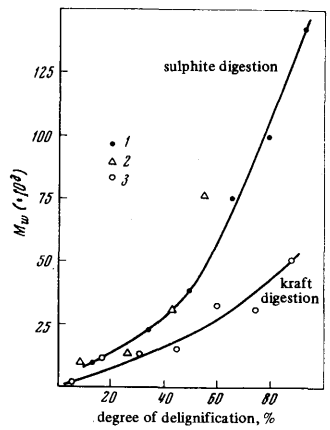

Figure 1. Variation of the molecular weights of the lignin preparations isolated by different methods with the degree of delignification of spruce wood[27,30,31]: *1*) acid sulphite digestion; *2*) hydrogen sulphite digestion; *3*) kraft digestion.

The separation of the resulting extracts on Sephadex G-50 led to the formation of three fractions (1) with molecular weight > 14 000; (2) with molecular weight from ~ 3000 to ~ 14 000; and (3) with molecular weight from 100 to ~ 3000. It was shown that as the proportion of carbohydrates removed increased, the relative quantity of lignin eluted from fraction 1 rose and the amount of lignin eluted from fraction 3 decreased. The relative

amount of lignin eluted from fraction 2 remained approximately constant at all stages of the carbohydrate removal. The observed increase in the ratio of high-molecular-weight to low-molecular-weight components as the carbohydrates are gradually removed was thought to show that wood lignin consists of at least two main components, which differ considerably in molecular weight and are localised in different parts of the cell walls of the fibres.

As regards the lignins isolated from plant tissue, their heterogeneity in molecular weight was shown by gel-filtration of lignin from mechanical grinding [34,35] and of alkali lignins [36], by fractionated dioxan-lignins [37,38] and by Brauns "native" lignin [39], by sulphite [40] and kraft [41] digestions of periodate lignin, and by many other investigations, consideration of which is not the task of the present review.

Hence the above results from studies of the molecular weight distribution of lignin during the delignification of wood by various methods (various digestion procedures, enzymatic isolation) has allowed us to pose the question of the existence of two types of natural lignin, which differ considerably in molecular weight. However, before examining the arguments for and against this hypothesis we must briefly characterise contemporary ideas about the distribution of lignin in the cell walls of plant tissue.

III. DISTRIBUTION OF LIGNIN IN THE CELL WALLS OF PLANT TISSUES

According to contemporary ideas concerning the anatomical structure of wood from coniferous species, the cell walls of moulded tracheids consist of two ontogenetically different structural parts: primary and secondary walls. The primary wall, which is the external sheath of the cell, plays an important part in the period of surface growth, whereas the secondary wall is formed after surface growth ceases. In turn the secondary wall consists of three layers with different optical properties (Figs. 2 and 3). In addition to the morphological subdivisions shown in Figs. 2 and 3, there are indications [46] of the existence of the so-called "warty layer", which covers the tertiary wall at the side of the lumen.

One of the first attempts to investigate the quantitative distribution of lignin in the cell wall was made by Ritter [47]. With the aim of removing the carbohydrate components, he treated 3 mm sections of wood with sulphuric acid according to the standard Klason method for determining lignin and found that middle lamella lignin and cell wall lignin could be distinguished in wood: the former retains the initial wood structure after removal of carbohydrates but the second is structureless. A mechanical separation of the lignin residue thus obtained showed that ~ 75% of the wood lignin is localised in the middle lamella, and ~ 25% in the cell wall and that the lignins localised in these two sites of the plant tissue differ significantly in the methoxy-group content (Table 8). Although the low methoxy-group content shows that the purity of the preparations is insufficient the fact that they are isolated under similar conditions and at the same time differ so much in the methoxy-group content is thought to show a significant difference between the middle lamella lignin and the cell-wall lignin.

On taking into account the volume occupied by the middle lamella in the wood tissue, Ritter was doubtful about the reliability of the values he had obtained which characterise the quantitative distribution of the lignin. The results obtained during this investigation enabled Ritter [48] to conclude that only half of all the wood lignin is localised in the middle lamella. However, in 1934 Ritter [49] confirmed his initial conclusion that the main mass of the lignin is localised in the middle lamella. Subsequently, this conclusion was confirmed in an investigation made by Harlow[50].

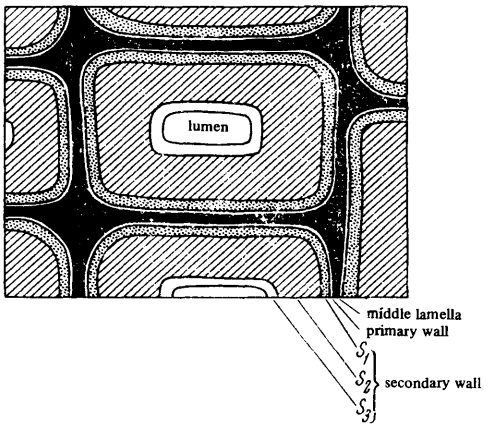

Figure 2. Transverse section of moulded tracheids of wood from coniferales species [42-44]. On the diagram are marked: the middle lamella or intercellular substance; the primary wall; the secondary wall, consisting of three layers: outer or external (S_1), middle or central (S_2), and internal (S_3); the lumen or cell cavity of the fibre.

The results obtained by Ritter and Harlow are evidently connected with the incomplete separation of the two types of lignin, since the mechanical method used for the separation is extremely imperfect, and also with the incomplete removal of carbohydrates, which is evident from the low concentration of methoxy-groups in the lignin preparations mentioned above.

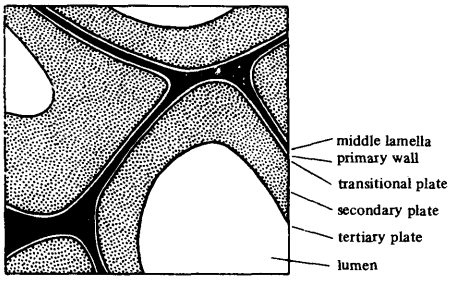

Figure 3. Transverse section of moulded tracheids of coniferales species [45].

Bailey [51,52] used a micromanipulator to separate 0.5 mg of the middle lamella from Douglas fir wood and found that the preparation isolated contained lignin 71, pentosans 14, cellulose 4%. Lange [53], using an ultraviolet microscope,

calculated that the weight concentration of lignin in the secondary cell wall amounted to 10–20%, and that in the middle lamella to 60–90%. The mean values obtained from 50 measurements were 16 and 73% respectively, and he suggested a gradual decrease in the lignin concentration from the middle lamella to the lumen. A series of investigations [54–56] showed that the distribution of lignin in the cell wall was more uniform than according to Lange's suggestion. The results of electron microscope investigations [57–59] of preparations of wood from which the carbohydrate components had been removed by various chemical treatments or by the action of enzymes showed that the distribution of lignin in the secondary cell wall is non-uniform; the lignin concentration is higher in the inner layer (S_3) close to the lumen and in the outer layer (S_1) adjacent to the primary wall.

Table 8. Distribution of lignin between the secondary cell wall and the material of the middle lamella [47].

Characteristic being studied	Red alder			Cuban white pine		
	secondary cell wall	material of middle lamella	total quantity	secondary cell wall	material of middle lamella	total quantity
Lignin, % of wood	7.3	19.5	26.8	6.9	23.4	30.3
Lignin, % of total lignin in wood	27.3	72.7	—	22.7	77.3	—
Methoxyl groups in Lignin, %	4.8	13.6	—	4.3	10.8	—

Investigations into the distribution of lignin in cell walls of plant tissues, published up to 1963, were examined in detail in the reviews of Northcote [60], and of Milyutina and Sergeeva [61].

The problem of the quantitative distribution of lignin in cell walls of plant tissues was critically examined by Berlyn and Mark [62], who emphasised that the results of Bailey and Lange are diametrically opposed to those of Ritter. Noting that the volume of the fractions of the middle lamella and primary-wall substances make up only 10–12% of the volume of the plant tissue, Berlyn and Mark calculated that even if this region consisted entirely of lignin it could not contain more than 40% of the total wood lignin. This surmise found experimental confirmation during an investigation by Goring and coworkers [63]. The method they employed was a combination of ultraviolet microscopy and densitometric analysis of negatives obtained by ultraviolet photomicrography. A special detailed examination of this method [64] showed that its use was well-founded, since when certain experimental conditions are satisfied the method enables the concentration of lignin in the various parts of the cell wall to be determined with sufficient accuracy. Furthermore, it is noteworthy that these investigators [63] calculated the concentration of lignin in the secondary wall by two methods: (1) on the basis of the relative ultraviolet absorption and the volumes of the fractions of different parts of the cell wall, and (2) directly from the absorption in the ultraviolet, using the Lambert–Beer law. The values obtained by the two methods showed good agreement, which also shows the reliability of their method.

Table 9 gives some results obtained by Goring and coworkers and shows that the middle lamella material is more lignified than that of the secondary wall, but despite this it contains only an insignificant proportion of the total lignin of spruce wood.

Table 9. Distribution of lignin in spruce tracheids [63].

Wood	Morphological differentiation*	Relative absorption of UV	Total fraction, %	Lignin, % of total lignin in wood	Lignin concn., g per g wood
Early	SW	1	87.4	72.1	0.225
	ML (r) (t)	2.21	8.7	15.8	0.497
	ML (cc)	3.77	3.9	12.1	0.848
Late	SW	1	93.7	81.7	0.222
	ML (r) (t)	2.7	4.1	9.7	0.60
	ML (cc)	4.5	2.2	8.6	1.0

*SW = secondary wood; ML middle lamella; r radial direction; t tangential direction; cc cell corner.

Scott and Goring [65] also used ultraviolet microscopy in conjunction with densitometric analysis of the ultraviolet photomicrographs obtained in investigating the concentration of lignin in the S_3 layer of wood of coniferous species.

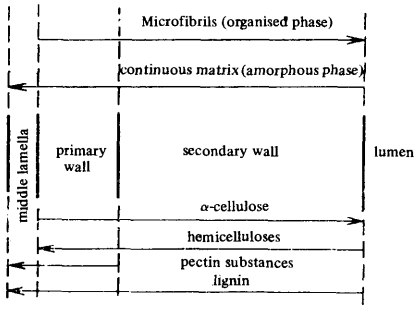

Figure 4. Distribution of the constituents of moulded cell walls. The arrows show the direction of the increase in the relative concentrations of the individual components [60].

Their results showed that in trunk wood a uniform distribution of the lignin in the secondary wall is usually observed. On the other hand, in the wood of the branches a high concentration of lignin in the S_3 layer is often observed.

Hence the above results show convincingly that the distribution of lignin in the cell walls of plant tissues is

non-uniform, and it is interesting to note that according to the results of several investigators [66-69] non-uniformity is also observed in the distribution of the carbohydrate components (hemicelluloses and cellulose) of plant tissue.

In ending the examination of the problems associated with the distribution of lignin in the cell walls of plant tissues, it is noteworthy that according to Northcote's views [60] the cell wall can be regarded as a two-phase system consisting of microfibrils immobilised in a continuous matrix. The microfibrils are concentrated close to the lumen and their density falls in the direction towards the outer parts of the cell, where the other phase prevails. Northcote proposed the following classification of the material of the cell wall:

1. Continuous matrix: (a) pectin substances; (b) lignin; (c) possibly, polysaccharides of the hemicellulose group.

2. Microfibrils: (a) polysaccharides containing glucose (cellulose); (b) polysaccharide (polysaccharides) containing xylose; (c) a polysaccharide (polysaccharides) containing mannose; (d) possibly, polysaccharides of the hemicellulose group.

The scheme presented in Fig. 4 is a representation of the distribution of the various components of the cell wall of plant tissue.

In conclusion, we must note that in comparison with coniferous woods the wood of deciduous species exhibits a more complex anatomical structure and also differs in the nature of the distribution of the lignin in the plant tissue [70].

IV. SOME ASPECTS OF THE HETEROGENEITY OF NATURAL LIGNIN

As stated above, the results obtained during experiments on the delignification of wood, allowed the problem of the existence of two types of natural lignin differing significantly in molecular weight to be settled. However, the solution of the problem of the homogeneity or heterogeneity of lignin not isolated from plant tissue is hindered by the impossibility of an unambiguous interpretation of the results examined in Section II. This is primarily because the use of acids or alkalis during the wood delignification processes considered above leads to more or less significant changes (on the one hand, hydrolytic; on the other, condensation) in the natural lignin, which change its structure significantly [28]. It is now impossible to speak with complete certainty about the absence of depolymerisation or condensation changes in the lignin even in its enzymatic isolation from the wood [33], which is the mildest method of those examined in Section II. Hence the heterogeneity, according to molecular weight, of the lignins isolated from wood by various methods may be due to the heterogeneity of the natural lignin or may be secondary, being the consequence of condensation or hydrolysis of the lignin during isolation.

In this connection other aspects of the problem of the heterogeneity of natural lignin which are of some interest and which can assist in presenting a more complete, even if more complex, picture of the contemporary state of this problem must be considered.

The non-uniformity of the distribution of lignin in plant tissue, considered in Section III, enabled certain investigators [27,30,33] to suggest the localisation of lignins with different molecular weights in different parts of the cell walls of wood tissue. The arguments of these investigators were based on a series of propositions.

According to contemporary ideas [71-74] the first traces of lignification are observed in the primary wall in the cell corners, then the process of accumulation and deposition of the lignin is extended to the middle lamella and throughout the entire primary wall, subsequently into the corners of the middle lamella of the cell, and finally, into the secondary wall (layers S_1, S_2, and S_3, successively, see Fig. 2). Starting from this, it is logical to suggest that the molecular weight of the lignin will be greatest at those parts of the cell wall, where the concentration of the lignin precursors is highest and consequently the degree of condensation polymerisation is increased. Such parts of the cell wall are the primary wall and the middle lamella.

At the same time, according to Cowling's results [75], obtained in the enzymatic isolation of lignin with brown rot fungus, the micro-organisms initially occupy the lumens of the cells of the wood tissue. It is logical to assume that in this connection the enzymatic "digestion" of carbohydrates takes place gradually in the direction of the middle lamella and consequently the lignin in the earlier stages of the enzymatic decomposition of the wood is extracted from the secondary layer and in the later stages from the middle lamella. Such a sequence of enzymatic action is shown by several investigators [45,76,77]. On this basis, Brown and coworkers [33] assumed that the low-molecular-weight lignin extracted in the initial stages of the enzymatic removal of carbohydrates is extracted from the middle lamella. The stated distribution of lignins with different molecular weights in the cell walls will favour a gradient in the size of the spaces between the microfibrils and the distances between the cellulose macromolecules in the amorphous regions from the central plate substance through the secondary wall to the lumen [53]. The electron microscope studies mentioned above [57-59] showed that the greatest density of lignin is observed in the middle lamella, the primary wall, and the S_3 layer. In the S_2 layer of the secondary wall the lignin exists as a branched three-dimensional lattice which immobilises the carbohydrate chains, which exhibit crystal structures. Furthermore all the investigators noted an obvious orientation of the lignin in the S_1 layer.

Finally, as a result of the investigation of the path of penetration of various liquids into wood and of the influence on this process of morphological factors, Wardrop and Davies [78] found that after penetration into the lumens of the cells the reagents used diffuse through the cell walls so that the middle lamella and especially the regions of the cell angles of the middle lamellas are the last parts which react with these agents. In the digestion of wood the path of penetration of the digestion solutions stayed the same but the rate of passage was greatly increased. These results give a basis for suggesting that low-molecular-weight lignin isolated at different stages of the delignification of wood by different methods (see Section II) is localised in the secondary wall, but the high-molecular-weight lignin is localised in the middle lamella.

A special investigation of the topochemistry of the delignification of spruce wood during industrial digestions showed the following regularities [79]. In the early stages of kraft and acid sulphite digestions the lignin is preferentially removed from the secondary cell wall. After ~50% delignification the lignin of the middle lamella is rapidly dissolved, leaving the residual lignin in the secondary wall. In the neutral sulphite digestion the removal of lignin from the secondary cell wall and middle lamella proceeds with approximately the same rates up to 50% delignification. Approximately analogous topochemical models of delignification were observed in kraft and neutral sulphite diges-

tions of birch wood [74]; in the early stages of the digestions preferential delignification of the secondary walls of the fibres and vessels. It is interesting to note that the sequence of the delignification of the various morphological parts of the cell wall of both spruce [79] and birch [74] wood in the order of the digestion processes used is: SW > > ML(cc) > ML(r)(t) (for symbols see Table 9), opposite to that examined above for the deposition of lignin during the lignification of plant tissue.

According to some results [74,79], the above morphological differences in the rate of delignification are not connected with the diffusion of the active reagent into the cell wall or with the diffusion of lignin macromolecules from the cell walls, but are due evidently to the different stability of the lignins to the actions of the digestion solutions. Were the morphological structure of the cell the main factor affecting the rate of delignification, it could be expected that the sudden breakdown of the wood structure (for example, as a result of the compression treatment of the wood at high temperature) leads to a considerable change in the rate of delignification. However, as the investigations of Yean and coworkers [80] have shown, preliminary treatment of spruce and birch sawdusts at pressures up to 35 155 kgf cm^{-2} and temperatures up to 200°C hardly altered the rate of delignification. Analogous results were obtained by Kleinert [81], who showed that preliminary compression of the wood had no effect on the absorption of SO_2 nor on the delignification in sulphite and kraft digestions. These results show that since the changes in the morphological structure of the cells have no significant effect on the rate of delignification of wood, the rate-determining factor for the dissolution of lignin in the various morphological parts of the cell wall is not its accessibility but the chemical structure of the lignins in these regions, which also determines their different degree of stability to the action of digestion solutions.

The mathematical model for the degradation of a three-dimensional gel developed by Szabo and Goring [82], applied to the delignification of spruce wood in kraft and acid sulphite digestions is thought [82] to confirm this assumption. In their calculations Szabo and Goring started from the assumption that the degradation of a three-dimensional gel is a reversible process in relation to trifunctional polycondensation, the theory of which was propounded by Flory [83]. According to this theory, the polycondensation of monomers which contain more than two functional groups leads to the formation of a three-dimensional lattice polymer. A characteristic feature of the three-dimensional polycondensation is the sudden formation of an infinite lattice observable at the point of gel formation. After this a high-molecular-weight three-dimensional lattice polymer (the so-called "gel-component") and a low-molecular-weight soluble product (the so-called sol-component) are present in the system, but a sharp separation into these components is not observed: the particles of the sol enclose the infinite lattice of the gel. With further condensation the amount and molecular weight of the sol component decrease as a result of the selective addition of its coarser and more complex particles to the infinite lattice of the gel-component, According to the model developed by Szabo and Goring, in the degradation of the three-dimensional gel initially low-molecular weight fragments are formed, which are distinct from the infinite lattice of the gel owing to the breaking of the intramolecular transverse bonds. In the later stages of the degradation the gel will "break up" and give coarser fragments of soluble lignin. In this model Szabo and Goring started from the assumption of the presence of two structurally different gels, one of which corresponds to the secondary wall lignin, the other to the lignin of the central lamella. The quantities predicted on the basis of the model developed by Szabo and Goring agree well with the experimentally obtained topochemical model of the delignification of spruce wood [79] and also with the molecular weight distribution of lignin in its isolation in acid sulphite [27] and kraft [31] digestions of spruce wood.

An analogous condensation was proposed by Elton [84] on the basis of a kinetic investigation of the delignification of wood of the loblolly pine during neutral sulphite digestion. As a result of the investigations it was found that 8–11% of the lignin is removed at an appreciably greater rate than the remaining lignin. This difference in the rate of delignification in the initial and subsequent periods of digestion was explained primarily on the basis of the molecular weight distribution of the lignin in the wood, and also on the basis of the diffusion of the reaction product and the physical availability of the lignin in the plant tissue. Elton assumed that the low-molecular-weight lignin dissolves slowly after sulphidation, and the rate of delignification in the initial digestion period is determined by the rate of sulphitation. On the other hand, for the dissolution of the remaining high-molecular-weight lignin its hydrolysis to finer fragments is necessary, which also determines the rate of delignification in the subsequent period of digestion.

In ending our examination of the problems associated with the topochemical delignification of wood during industrial digestions mention must be made of the work of Jayme and Torgersen [85], who investigated the topochemical delignification in sulphite and sulphate digestions. Their ultraviolet microscopical investigation into the partial delignification of spruce wood showed that in the sulphite digestion (loss of 27.5% of the initial lignin) the concentration of lignin in the secondary cell wall hardly altered and almost all the dissolved lignin was removed from the middle lamella. The delignification began with the material of the middle lamella and proceeded in the direction of the lumen. In sulphate digestion (removal of 29.8% of the initial lignin) a considerable proportion of the lignin was removed from both the secondary wall and from the middle lamella. The delignification in this instance began simultaneously from the middle lamella and the lumen.

In the present review we have not spent time on an examination of the occasionally contradictory results of the early investigations on the topochemistry of the delignification of wood [78,86–97]. However, a comparison of only two late investigations in this field (Goring and coworkers [79] and Jayme and Torgersen [85]) who used the same method but arrived at different conclusions shows that this problem requires further experiments to be made.

In conclusion, it is interesting to trace the evolution of Goring's opinions on the heterogeneity of natural lignin. On the basis of investigations of the molecular weight distribution of the lignins isolated during acid sulphite [27] and bisulphite [30] digestions, he suggested the presence in spruce wood of two types of lignin: low-molecular and high-molecular-weight, localised in different parts of the cell wall. Later experiments [79] on the topochemistry of the delignification of spruce wood, which showed that in the early stages of sulphite and kraft digestions there is preferential delignification of the secondary wall, allowed Goring [98] to suggest that the low-molecular-weight lignin is localised in the secondary wall. Finally, the theory of the degradation of a three-dimensional gel, developed by Szabo and Goring [82] led them to the conclusion that low-

molecular-weight lignin, which, dissolves in the early stages of the digestion, is formed as the result of the degradation of both lignin gel localised in the secondary wall and also the lignin gel of the middle lamella. They assume that instead of low- and high-molecular weight lignins we must speak of the structurally different lignin of the secondary wall and the lignin of the middle lamella.

V. HETEROGENEITY OF LIGNIN IN RELATION TO ITS BONDING WITH THE OTHER COMPONENTS OF PLANT TISSUE

In conclusion yet another aspect of the problem of the heterogeneity of natural lignin must be mentioned, one which is connected with the existence of lignocarbohydrate bonds in plant tissues [99].

In 1958 Aaltio [100,101] published the results of an extensive investigation of the type of bonding of lignin with other components of plant tissue. He undertook a series of nine butanol digestions of aspen wood. Fine sawdust, previously extracted with acetone was digested with neutral buffered butanol–water mixture for 4 h at 158°C. Each successive digestion was carried out on the residue from the previous one. The solubility of the wood was traced by analysis of the insoluble residues and digestion solutions. Table 10 gives some of the results of the investigations.

Table 10. Some results obtained in successive digestions of aspen wood with buffered aqueous butanol [100].

Digestion No.	Ratio of dissolved lignin to dissolved pentosane-uronids	OCH_3 groups in dissolved lignin, %		Digestion No.	Ratio of dissolved lignin to dissolved pentosane-uronids	OCH_3 groups in dissolved lignin, %	
		found	calculated			found	calculated
1	1.05	21.4	21.7	6	0.59	—	15.3
2	0.75	—	21.3	7	0.55	15.0	15.0
3	0.77	20.1	20.2	8	0.54	—	15.0
4	0.73	—	21.4	9	0.55	14.9	12.0
5	0.74	17.9	17.9				

The results led Aaltio to the conclusion that aspen wood consists partly of homogeneous ligno-carbohydrate complexes. According to his interpretation, during the first five digestions there is a gradual action of the digestion solution on the middle lamella, which leads to the separation of a highly methoxylated lignin and pentosan uronides in the ratio ~ 0.75. After dissolution of all the middle lamella defibrisation of the material takes place and in subsequent digestions the secondary cell wall is subjected to the action of the digestion solution. This leads to the separation of lowly methoxylated lignin and pentosan uronides again in a constant ratio (~ 0.55), which, however, differs from the ratio found for the dissolution of the middle lamella. It is noteworthy that according to Aaltio, the greater part of the lignin in the complex isolated from the middle lamella is in the free state and does not have chemical bonds with the carbohydrate components. This assumption of Aaltio agrees with the conclusions of other investigators.

Thus, according to Björkman's ideas [102], the lignin in the growing plant tissues can be divided into two fractions in respect of its bonding with hemicelluloses. One fraction has a very small number of bonds with hemicelluloses or none at all and in all probability is localised in the middle lamella. This fraction is isolated under mild conditions and corresponds to the lignin of mechanical grinding obtained by Björkman's method. The other fraction is firmly linked with hemicelluloses and can be isolated by more severe methods. This fraction corresponds with the lignocarbohydrate complex obtainable by the Björkman method. The ratio between these fractions is ~1:1. On the basis of experiments on the fractionation of hydroxyethylated wood (previously ground in a ball mill) dissolved in dimethylformamide, Brownell and West [103] also concluded that approximately three-quarters of all the lignin in wood is chemically bound with carbohydrates. About one-quarter of the lignin can be easily separated from the carbohydrates. They assume that this fraction is not linked with the carbohydrates by a hydrogen bond although it is quite possible to assume that these bonds are broken at the time the wood is ground in the ball mill. As a result of an investigation involving oxidation of wood with hydrogen peroxide, Berlin [104] concluded that the lignin localised in the middle lamella is of higher molecular weight and is chemically unconnected with the polysaccharides. Tishchenko [105] concluded, on the basis of results on the stepwise ozonation of spruce wood in ethyl acetate, that in spruce there are both lignin unconnected chemically with carbohydrates (not less than 43% of all the lignin) and lignin thus connected.

It is interesting to note that in 1934 Boyarkin [106] made a microchemical examination of the sclerin-chemical fibres using two widely known colour reactions: phloroglucinol and the Mäule reaction. As a result of this, he found the presence of different microchemical reactions at different elements of the lignified tissues. Thus a characteristic reaction with phloroglucinol + conc. H_2SO_4 is shown only by the primary walls of neighbouring cells with intercell substance between them, whereas the Mäule reaction is characteristic only for the secondary cell wall‡. These results enabled him to suggest the existence in the lignified tissue of two components of lignin, designated respectively as "F" and "M". Later Bardinskaya [112] found that alkaline extraction of lignified material alters the microchemical reaction significantly: after extraction with alkali (0.5 *N* NaOH) the vessels which had retained their form were not stained by phloroglucinol + H_2SO_4. Evidently this is because the alkali extracts that part of the lignin which is responsible for the phloroglucinol reaction of the lignified fibres. On the basis of this a scheme for the isolation of both components of the lignin was proposed; it involved the alkaline extraction of the plant material, previously extracted with alcohol–benzene mixture (isolation of component "F") and then the acid hydrolysis of the residue (isolation of component "M"). The fractions obtained were quite different in elementary and functional composition (Table 11).

According to Bardinskaya [116], fraction "F" is the most "mobile" part of the lignin, less firmly connected with the other components of the cell wall. The remaining part of the lignin (fraction "M") is evidently more strongly

‡It has been repeatedly suggested [107-111] that this difference in the colours in the microreactions on the lignin is because some of the histochemical reactions (including that of phloroglucinol) are characteristic for the guacyl residues of the lignin and the second group (including the Mäule reaction) for the syringyl residues.

bound to the polysaccharides components of the cell wall and therefore is not extracted by alkali under the conditions employed. Bardinskaya assumes that the two fractions also differ in molecular weight. In addition it has been suggested [117,118] that there is the possibility of the existence of different paths of biosynthesis for the two components of the lignin. Later Furst [119] investigated differential conduction systems and the dynamics of the accumulation of lignin in the elements of the xylem at various stages of the development of leaves of certain types of onion from the moment of germination of the seed up to 4–6 month seedlings. He showed that the "F" component is formed earlier than "M" lignin, and if the "F" component starts to be deposited at the side of the middle lamella and primary wall, then the component "M" is mainly deposited on the inner (at the side of the cavity) envelopes of the leaf tracheids.

Table 11. Characteristics of the lignin fractions isolated from sugar beet stalks [114,115].

Fraction	Yield of lignin, % of initial raw material	Present, %				Yield of aromatic aldehydes after nitrobenzene oxidation of the lignin, % of lignin
		C	H	N	OCH_3	
Lignin "F"	0.59	57.32	6.62	3.71	14.05	6.0
Lignin "M"	7.25	58.32	6.02	0.9	18.46	4.8

The hypothesis of the existence of two types of lignin received confirmation as a result of Lüdtke's chemical investigation [120] of the best fibres of various plants. According to his results, these lignins are distinguished in localisation in the cell wall of the plant. The major fraction of the lignin is localised in the middle lamella; the second fraction, which makes up 10–30% of all the lignin, is localised in the primary and secondary cell walls and is chemically bound with carbohydrate material. These fractions differ somewhat in elemental composition and content of OCH_3 groups.

In conclusion, mention must be made of the results of an investigation by Matsukura and Sakakibara, published recently [121]. They isolated from the wood of the spruce (*Picea jezoensis*), ground in a vibromill, the mechanically ground lignin (MGL) and lignin-carbohydrate complex (LHC) (by extraction with dimethylsulphoxide) according to Björkman's method. The MCL and LHC and the residue were subjected to ethanolysis and also to oxidation by $KMnO_4$ or nitrobenzene in alkaline medium. The quantity of degradation products was found by gas chromatography.

The oxidation of LHC by permanganate led to the production of a very small quantity of degradation products: 1.78% (reckoning from the lignin in the LHC) veratric acid, 0.46% isohemipinic, and 0.25% dehydrodiveratric acid. As a result of the ethanolysis of LHC, monomeric products were obtain in good yield: guacylacetone, methyl vanyloyl ketone, and 2-ethoxy-1-guacylpropan-1-one. From these results it was concluded that bonds of the arylglycerol β-aryl ethers type predominate in the lignin present in the LHC.

The oxidation of the wood residue with permanganate led to the production of the same acids in good yields: 9.88, 3.46, and 3.43% on the lignin; at the same time as a result of ethanolysis only insignificant amounts of the monomeric "Hibbert ketones" were obtained. These results are thought to show the presence in the wood residue of a large quantity of condensed chains of lignin. The results of alkaline nitrobenzene oxidation of all three specimens showed small but distinguishable differences between them.

Matsukura and Sakakibara assume that the above results convincingly show the heterogeneity of the chemical structure of the lignin. According to the results obtained the LMP isolated by the Björkman method exhibits a structure intermediate between the other two preparations and in this connection they think that it cannot be regarded as a model for all the lignin of wood.

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The investigations of the last 10–15 years which we have considered above enable us to acknowledge to the first approximation the presence in plant tissue of two types of lignin, which differ in molecular weight, in localisation in the cell wall, in bonding with other components of the plant tissue, and also in the topochemical behaviour in the different processes for the digestion of wood.

The results of these investigation confirm the hypotheses, repeatedly expressed earlier, concerning the heterogeneity of natural lignin. Here we must first note Klason's hypothesis [122–124] concerning the existence in spruce wood of α- and β-lignins. He formulated this hypothesis on the basis of experiments on the precipitation with 2-naphthylamine hydrochloride of the lignosulphonic acid obtainable in the sulphite digestion of wood. Later Holmberg and Wintzell [125] and also Hibbert and coworkers [126] reported the presence of two fractions in alkali lignin which could be isolated from black alkali after the soda digestion of spruce wood. Proof of the heterogeneity of natural lignin is also provided by the results of the fractionation of a series of preparations that have been isolated: formic acid lignin isolated from birch wood [127], ethanol-lignin from wood [128–130], acetic acid [131] and butanol-lignins [132–135], isolated from various wood species; lignin isolated by hydrogenolysis of maple wood [130,136], lignins extracted from oat and wheat straw by methylcellolsolve + HCl [137]; lignins isolated from bamboo [138] and aspen [139,140] woods by a hydrotropic method, and also enzymatically isolated lignins [141]. Finally, mention must be made of the hypothesis of Purves [142], who assumed that the molecular weight and the ratio of the "free" and "combined" lignins in the plants can vary not only with the type of plant but also with growth and the growing conditions. These investigations have been partly considered in Lebedev's review [143].

As regards the practical recommendations [74,79] which can be made from the existence of different types of natural lignin, clearly of most importance would be the finding of a delignifying agent which exhibits specific action towards the middle lamella, which probably consists mainly of lignin. This would lead to the obtaining of a fibrous mass in very high yield which could then either be used as such or be subjected to further delignification for obtaining a desired type of fibre.

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Catalytic Disproportionation of Unsaturated Hydrocarbons

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The review considers the data at present available on the disproportionation reaction† of olefins. The practical value of this versatile reaction, which opens up new pathways for synthesis of a wide variety of unsaturated hydrocarbons, is noted. The applications of the reaction to dienes and acetylenes are also considered.
Studies using various heterogeneous disproportionation catalysts have been described, together with simple process parameters (catalyst activity, temperature, pressure, etc).
Much attention has been devoted to the applications of homogeneous catalytic systems in the disproportionation of olefins and to the characteristics which distinguish them from heterogeneous catalysts. Problems concerned with the reaction mechanism and its stereochemical features are discussed.
The bibliography includes 92 references.

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I. INTRODUCTION

The most important and interesting reactions in organic chemistry discovered in the last decade undoubtedly include the disproportionation of olefins. This reaction apparently constitutes a new field in the chemistry of unsaturated compounds.

According to the first patent data [1-4] and more detailed subsequent studies [5,6], acyclic olefins can be converted in the presence of catalysts into higher and lower homologues:

$$\underset{50\%}{2\,RCH{=}CHR'} \rightleftarrows \underset{25\%}{RCH{=}CHR} + \underset{25\%}{R'CH{=}CHR'}.$$

The olefins with a smaller and larger number of carbon atoms (compared with the initial substance) are formed in almost equal molar amounts. The degree of conversion is limited by the thermodynamic equilibrium.

The new catalytic reaction immediately attracted attention, which led initially to the publication (starting in 1964) of numerous patents dealing with the search for the best disproportionation catalysts, the development of suitable conditions for the process, and its practical applications.

The considerable interest in the disproportionation of olefins is due to the versatility of this reaction and the consequent increase in the number of methods for the chemical processing of unsaturated hydrocarbons.

Some of these possibilities will be mentioned here. The disproportionation reaction constitutes an extremely effective means for the preparation of olefins with various structures, many of which serve as the starting material in many manufacturing processes. For example, the disproportionation of propene leads to the preparation of very pure ethylene and straight-chain butenes—olefins which are used in the large-scale manufacture of various valuable products (polyethylene, vinyl chloride, styrene, ethylene oxide, butadiene, butyl alcohols, and others).

The disproportionation of straight-chain butenes yields straight-chain pentenes—the starting material for the synthesis of isoprene. For the synthesis of olefinic hydrocarbons, disproportionation is particularly promising because many types of the initial olefinic raw material can be provided by the petrochemical industry.

An unusual feature of the reaction is the mutual disproportionation of two molecules of different olefins. In particular, if one of the olefins is ethylene, the reaction (the so called ethenolysis) makes it possible to convert olefins with an inner multiple bond into α-olefins [6-8].

The application of disproportionation to cyclo-olefins merits particular attention, since it provides a new synthesis of macrocycles [9-11]. Mutual disproportionation of cyclic and alicyclic mono-olefins leads to the formation of diolefins [12,13].

It is noteworthy that the disproportionation reaction is not characteristic solely of mono-olefins. Recently the disproportionation of dienes [14] and alkynes [15] was discovered. It is also likely that olefins with other than alkyl substituents can also be disproportionated, as shown by the disproportionation of stilbene [16]. All these findings suggest that the disproportionation process has general applicability and is characteristic of all unsaturated compounds.

An important feature of the reaction is the high purity of the products obtained, which could hardly be achieved by any other method of synthesis (especially with higher olefins).

A fundamentally new stage in the development of the disproportionation reaction has been the use of homogeneous catalytic systems [17-24], which exhibit an unusually high selectivity and stereospecificity. An industrial application of the disproportionation reaction has been achieved comparatively rapidly, particularly in the conversion of propene into ethylene and straight-chain butenes [25-27]. The first industrial apparatus for this process, which also included a system for the further conversion of straight-chain butenes into butadiene, was first used in Canada in 1966‡. The annual production

†In addition to the term "disproportionation", the terms "dismutation" and "metathesis" are also employed.

‡The process was patented by the Phillips Petroleum Co. under the name "Triolefin Process". [28]

from the apparatus with respect to the raw material (obtained from pyrolitic gas) was 31500 tonnes, the output of ethylene being 9000 tonnes and that of straight-chain butenes 22 700 tonnes[27]. Thus the problem of the utilisation of propene (the principal side product in the manufacture of ethylene), the demand for which lags behind its supply in the world markets[29], can be partially solved.

One can also point to other applications of the reaction which show promise for industry. For example, mixtures of ethylene and but-2-ene (disproportionation products of propene) can be usefully alkylated with isobutane[30,31]. The alkylated products thus obtained have a higher octane number than the alkylation products based on propene.

A combination of the cracking of petroleum raw material with olefin disproportionation and dehydrogenation processes and also with the isomerisation and polymerisation of olefins has been proposed in a number of studies[3, 32-35].

Thus the disproportionation of unsaturated hydrocarbons opens up new and interesting possibilities not only for preparative chemistry but also for chemical industry.

At the present time there are no publications in the USSR literature giving a systematic and general account of the advances in the disproportionation of olefinic compounds§. The aim of the present review is to fill this gap.

II. HETEROGENEOUS CATALYSTS FOR THE DISPROPORTIONATION OF OLEFINS

The range of metals whose compounds provide the basis of heterogeneous catalysts for the disproportionation of olefins was comparatively small until recently: these were mainly molybdenum, tungsten, and rhenium; the list has been appreciably expanded only in recent years, the following metals having been introduced: rhodium, iridium, osmium, ruthenium, niobium, tantalum, tellurium, lanthanum, thorium, vanadium, and tin.

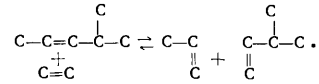
The most common catalysts are molybdenum, tungsten, and rhenium oxides deposited on alumina or silica gel. Among these the cobalt–molybdenum catalysts are outstanding because of their effectiveness, availability, and relative cheapness[1-8,37-57]. Their molybdenum oxide content is usually 1–15% (mainly 12–14%) and that of cobalt oxide is 1–5% (the optimum content is 2.5–3.5%). These catalysts are active over a very wide range of temperatures: from 20° to 400°C (the optimum range is 90 to 260°C); the pressure can vary from atmospheric to 140 atm. An industrial cobalt–molybdenum catalyst (11% MoO_3, 3.4% CoO, and 85.6% Al_2O_3)[5] showed a very high efficiency: for example at 205°C and a pressure of 32 atm, the conversion of propene supplied at a weight rate of 3.5–4.4 kg h^{-1} reached 42.4%, the selectivity being greater than 94%.

A chromium–molybdenum catalyst on alumina with somewhat better properties than the cobalt–molybdenum catalysts was proposed quite recently[52].

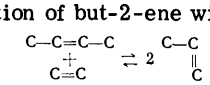
Tungsten oxide (usually 3% WO_3) also exhibits a high disproportionating activity[4,37,43-50,53-55]; however, this catalyst is effective at higher temperatures than the molybdenum catalyst (250–550°). Thus the maximum degree of conversion of propene (44.8%) in the presence of tungsten oxide is attained only at 427°C.[44,53] The use of tungsten oxide on silica gel for the synthesis of 2-methylbut-2-ene (the starting material in the synthesis of isoprene) by the disproportionation of a mixture of isobutene with but-2-ene or propene has been described[55]. For an isobutene conversion of 35%, the isopentene content in the C_5 fraction was 92–97% (450°C and 21 atm).

After the molybdenum and tungsten oxides, catalysts based on rhenium oxide (1–20% Re_2O_7) began to be employed[8,47-51,56-66]. They rapidly gained recognition owing to their activity, high selectivity, and resistance to catalytic poisons. Moreover, with rhenium catalysts it proved possible to carry out the reaction under milder conditions than on MoO_3 and WO_3: 20–100°C and atmospheric pressure. But-1-ene is converted into ethylene and hex-3-ene with a selectivity of 95.5% at a temperature as low as 25°C, the conversion being 38%.[64]

Rhenium catalysts yielded excellent results in ethenolysis[8,64]; in particular, 3-methylbut-1-ene and propene were obtained from 4-methylpent-2-ene and ethylene in 93% yield for a 94% conversion of the initial higher olefin (25–140°C and atmospheric pressure)[64]:



The disproportionation of but-2-ene with ethylene,



under the same conditions gives a 100% yield of propene (the conversion with respect to but-2-ene is 55%).

The disproportionation of readily polymerised secondary and tertiary olefins with alkyl and aryl substituents has been achieved in the presence of Re_2O_7/Al_2O_3.[65,66]

Apart from the molybdenum, tungsten, and rhenium oxides mentioned above, the carbonyls of these metals deposited in an amount of 5–10% on alumina are also employed as catalysts for the disproportionation of olefins[5,35,45,67]. The carbonyl catalysts are active at fairly low temperatures (100–150°C) and are particularly effective in the disproportionation of higher olefins. The dependence of the activity on the nature of the metal is the same as for the oxides, i.e. $Mo(CO)_6$ and $Re(CO)_{10}$ show the highest activity. For example, whereas the conversion of but-1-ene in the presence of $Mo(CO)_6/Al_2O_3$ (120°C and 35 atm) is 10% and that of pent-1-ene 60%, in the presence of $W(CO)_6/Al_2O_3$ the conversions of these olefins are 7 and 44% respectively[5].

Attempts were made to use alumina, silica gel, and aluminosilicates promoted with molybdenum and tungsten sulphides (2–10%) for the disproportionation of C_3–C_{20} olefins[49,68]. However, these catalysts proved to be relatively inactive over a fairly wide temperature range (65–535°C) (for example, the conversion of propene did not exceed 1.3%).[68]

Among catalysts including other metals in their composition, those with lanthanum, rhodium, iridium, osmium, and tin oxides on alumina are known[69]. They all exhibit very low disproportionating activity (for example, the maximum conversion of propene at 350°C was achieved in the presence of RhO_3 but amounted to only 6%). According to patent data[70-73], the disproportionation catalysts are also promoted by tantalum, tellurium, niobium, ruthenium, vanadium, and thorium (mainly as the oxides). Niobium, tantalum, and tellurium oxides proved to be the most effective among these. However, a quantitative comparison of the activities of these catalysts is difficult because of the differences in the test conditions.

§During the preparation of this paper, Bailey's review was published[36].

Recently it was discovered [74,75] that olefins are appreciably disproportionated on alumina alone. The conversion of propene in this process was 0.1–8.5% depending on temperature; a higher conversion was achieved at 400°C and atmospheric pressure, the selectivity being 12% with respect to ethylene and 58% with respect to straight-chain butenes.

The disproportionation reaction is probably very common in catalysis and accompanies many processes involving the formation or conversion of olefins in the presence of alumina. In particular, it has been shown [75] that disproportionation takes place in the dehydration of isopropyl alcohol [76] and also probably under the conditions of ethylene hydropolymerisation [77].

The principal parameters which determine the course of the olefin disproportionation reaction are catalyst activity, temperature, and contact time. Pressure apparently does not play a significant role (the reaction takes place without a change in volume); it has an effect only in consequence of a change in the density of the gases. The effect of these factors on the conversion and selectivity has been investigated in greatest detail for the disproportionation of propene [5,25,31,52,53,67,78,79] in connection with the development of the optimum conditions for the industrial process.

The kinetics of the disproportionation of propene on WO_3/Al_2O_3 (in a pilot plant) were examined [80] and it was shown that the reaction is between an adsorbed propene molecule and one from the gas phase (or physically adsorbed—Rideal's model). The rate of the process is limited by the rate of collision between the molecule and the catalyst surface. The apparent propene disproportionation energy is 21.6 kcal mole^{-1}.

However, the results obtained in a recent study [81] for the initial rate of the disproportionation of propene (in the presence of the cobalt–molybdenum catalyst) support another mechanism: the reaction takes place between two propene molecules adsorbed on the surface of the catalyst (the Langmuir–Hinshelwood model).

A thermodynamic calculation has been carried out on the disproportionation of propene and the equilibrium constants have been determined in the range 50–300°C. [82]

The activity of disproportionation catalysts, like that of catalysts in other processes, is determined mainly by the nature of the metal and the type of carrier; in addition, promoting additives, the method of preparation of the catalyst, and catalytic poisons have a considerable influence.

As already mentioned, transition metal (tungsten, molybdenum, and rhenium) compounds are best catalysts for the disproportionation of olefins. Cobalt [5,78], alkali and alkaline earth metals [6,41–44,49] and also compounds of Group VIII metals [49] have been recommended as promoting additives to oxide catalysts. Side reactions (isomerisation, coke formation, etc.) are mainly suppressed in their presence.

A general method for enhancing the activity of disproportionation catalysts consists in their preliminary activation by gases at 300–900°C (nitrogen, hydrogen, oxygen, carbon dioxide, carbon monoxide, helium, and dry air) followed by treatment with an inert gas (mainly nitrogen). Thus the conversion of straight-chain pentene after treatment of WO_3/SiO_2 with carbon monoxide increased by 36.5%. [43] The effect of preliminary treatment on the activity of disproportionation catalysts has been confirmed by infrared spectroscopy [79] [for $Mo(CO_6)/Al_2O_3$]. The effectiveness of the catalysts, in particular a rhenium catalyst, depends to some extent on the polarity of the solvent in which the oxide is dissolved for subsequent impregnation of the carrier [60]. When dioxan, methanol, and water were used, the degree of disproportionation of but-1-ene was 31.5, 29, and 24.6% respectively with molar selectivities in relation to $C_2 + C_6$ olefins of 95, 93, and 78.2%.

To improve the activity of the solid oxide catalysts, it is recommended that [72] they be treated in a hydrocarbon solution by the hydrides of organic derivatives of Group I, II, or III metals (for example with triethylaluminium).

Alumina, silica gel, and aluminosilicates were mainly employed as carriers, and less frequently aluminium, magnesium, titanium, zirconium, and calcium phosphates [31,70] and magnesium [4], thorium, and zirconium oxides [70]. The oxides of Group IV elements were employed for rhenium catalysts [58,59,62] and it was found that in the presence of Re_2O_7/SnO_2 the conversion of but-2-ene was higher by a factor of 10 compared with Re_2O_7/Al_2O_3 (other conditions being equal) [62]. One cannot rule out the possibility that carriers comprising the oxides of Group IV elements themselves catalyse the disproportionation reaction.

The conversion of olefins increases by 5–10% and the period of constant activity of the catalyst is doubled when the alumina carrier is first treated with a 0.001–10 N solution of an organic or inorganic acid (mainly hydrochloric and acetic acids) [45,48,51,63,67,69].

The problem of the effect of catalytic poisons on the activity of heterogeneous disproportionation catalysts is very important. The majority of different types of olefinic starting materials are obtained by pyrolysis or thermal cracking and contain numerous admixtures which deactivate the catalysts (water, hydrogen sulphide, oxygen and its compounds, and also alkynes and alkadienes). The presence of water or sulphur compounds in the starting material rapidly reduces the conversion of the olefins. For example, when propene is saturated with water, its conversion in the presence of WO_3/SiO_2 is reduced in 1 h to 10% and in the presence of sulphur dioxide to 16%, while hydrogen sulphide completely deactivates the catalyst [53]. The elimination of water and sulphur compounds under industrial conditions can be successfully achieved using molecular sieves [25].

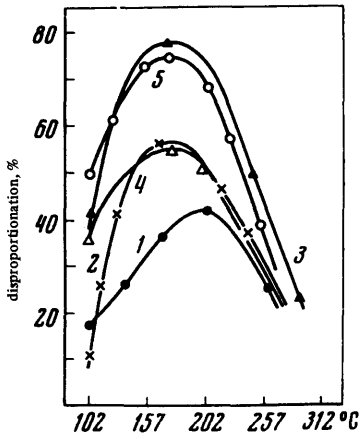
Alkynes and alkadienes, which form coke and polymer deposits on the catalysts, are also powerful catalytic poisons [43]. In this case the activity of the catalyst can be restored only by regeneration. The yield of coke is reduced by the addition of 2–4% of cobalt oxide to molybdenum oxide [5]. In addition, the olefinic starting materials may be subjected to preliminary purification, designed to remove acetylenes and dienes, by selective hydrogenation on industrial palladised catalysts [25].

Disproportionation in the presence of 10–60% of hydrogen is recommended as a method which eliminates the necessity for a careful preliminary removal of alkadienes from alkenes; at the same time the activity and the useful life of the catalyst increase appreciably [49].

The resistance of the catalyst to poisons increases with process temperature; however, as will be shown below, high-temperature conditions are undesirable for many reasons.

The presence in the olefinic starting material of paraffinic and cycloparaffinic hydrocarbons does not affect the reaction and therefore they can be used as inert diluents [5,43,48,53,69]. Thus a change in the concentration of propene in the starting material from 60 to 99% (the residue was propane) did not affect its conversion. This is very important, since there is then no need to concentrate the olefins before their disproportionation.

The effect of process temperature on the degree of conversion of olefins was investigated in the disproportionation of propene [5,25,52,53,82], straight-chain butenes [5,6], straight-chain pentenes [5], hex-1-ene [5], oct-1-ene [5] and other olefins [48,51,68]. In all cases the temperature dependence of their conversion is described by a curve with a maximum, which is typical of reactions the rate of which is limited by an equilibrium (see Figure).



Effect of temperature on the degree of disproportionation of olefins: 1) propene; 2) but-1-ene; 3) pent-1-ene; 3) hex-1-ene; 5) oct-1-ene.

Optimum temperatures correspond to the majority of the most favourable combinations of degree of conversion and selectivity, since after the attainment of the temperature of the onset of isomerisation and cracking, the efficiency begins to decrease rapidly. Thus, when the temperature is increased from 95° to 205°C ($CoO.MoO_3.Al_2O_3$ catalyst, pressure 32 atm), the conversion of propene increases from 17.9 to 42.6%. According to a thermodynamic calculation [82], a further increase of temperature should lead to increased conversion. Nevertheless, above 200°C the conversion fell to 14.6% (at 300°C), in all probability due to side processes and deactivation of the catalyst. The best combination of degree of conversion and selectivity for propene is achieved at 163°C.

Thermodynamically the disproportionation process is independent of pressure. [82] However, experimental data [5,43,52,53] show that an increase of pressure favours the process to some extent. Probably this effect may be explained by an increase of the concentration of the olefin on the catalyst surface, which in turn leads to an increase of the rate of reaction. It has also been noted that [43] a decrease of pressure (below 10 atm) in the disproportionation of higher olefins promotes the formation of products with a more branched chain than in the initial substances. In certain cases (particularly in the presence of MoO_3) an increase of pressure was accompanied by an increase in coke formation [43]. A pressure below 40 atm is usually optimum (for example, in the disproportion of propene it is 32 atm).

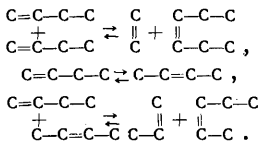
The space velocity at which the stream of starting material is supplied varies within wide limits probably only in the case of propene (between 10 and 130 kg h^{-1}) and does not influence appreciably the degree of conversion [25]. However, a further increase of space velocity (> 180 h^{-1}) leads to some decrease of the conversion of propene [52]. In the disproportionation of higher olefins, the rate of supply of the olefinic starting material plays an important role in determining the possibility of isomerisation, which usually becomes very appreciable at low flow rates of the starting material and almost disappears at high flow rates.

The contact time is related to pressure and space velocity and also depends on temperature and the activity of the catalyst. It can vary from 0.1 s to 120 min, the optimum time recommended being 0.1–60 s.

The main factor which precludes a 100% yield of the required products in the disproportionation of olefins is undesirable side reactions (isomerisation, cracking, polymerisation, condensation, and others), which inevitably occur to some extent on heterogeneous catalysts. However, by careful choice of conditions, the majority of side processes may be suppressed to an extremely insignificant level ensuring thereby a higher selectivity and conversion. The only reaction which cannot be completely eliminated is isomerisation.

It is noteworthy that the isomerising activity of the catalyst decreases more rapidly than its disproportionating activity [6]. Probably this is evidence that both reactions occur at different catalyst active centres. On this basis, isomerisation may be to a large extent suppressed by poisoning the acid regions of the catalyst (which are responsible for its isomerising capacity) by adding small amounts of alkali and alkaline earth metals [6,7,41–49], the effectiveness of the alkali metal ions increasing in the sequence sodium < potassium < rubidium < caesium [41]. When the catalyst is cautiously poisoned and appropriate conditions are chosen, it is possible to control the isomerisation reaction and to obtain pure olefins with a high degree of selectivity.

With this idea in mind, a detailed study was made of the disproportionation of straight-chain butenes [6], which can lead both to ethylene and hex-3-ene (from but-1-ene) and to propene and straight-chain pentenes (from but-2-ene):



By varying the reaction temperature, the rate of supply of but-1-ene, and the amount of sodium in the catalyst, it was possible to find the optimum conditions for both the disproportionation reaction (the formation of $C_2 + C_6$ olefins) and for isomerisation (the formation of $C_3 + C_5$ olefins). The highest selectivity with respect to $C_2 + C_6$ olefins (90.7%) was achieved in the presence of a cobalt–molybdenum catalyst treated with a 0.2 *N* solution of $NaHCO_3$ (140°C). An increase of temperature and a decrease of the rate of supply of but-1-ene promote its isomerisation to but-2-ene and hence an increase in the yield of $C_3 + C_5$ products.

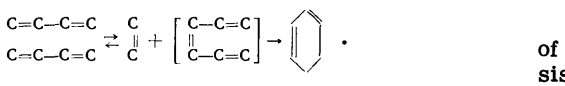
One of the important advantages of the olefins disproportionation process is the purity of the products. If one starts with a pure starting material, then theoretically pure alkenes should be obtained. However, in practice the reaction products are usually contaminated by impurities from various sources (the starting material and the regenerating gas), which are retained on the catalyst and are liberated in the subsequent working period. Moreover, another source of impurities is side reactions accompanying the disproportionation (isomerisation, cracking, hydrogenation, hydrogen transfer).

Nevertheless, the experience gained on an industrial apparatus for the disproportionation of propene has convincingly demonstrated that the majority of the sources of impurities can be controlled to some extent, so that the propene conversion products (ethylene and straight-chain butenes) do not require additional purification (the purity of of commerical ethylene, for example, can be easily raised to 99.9%).[25]

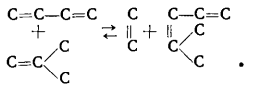
Not only mono-olefins but also dienes undergo the disproportionation reaction[14]. So far only heterogeneous catalysts for the process are known. In particular tungsten oxide deposited on silica gel (7% WO_3) with a small amount of sodium (0.19% Na_2O) catalyses at 538°C and atmospheric pressure the disproportionation of buta-1,3-diene, penta-1,3-diene, and also mixtures of these dienes with mono-olefins (propene, butenes).

The conversion of dienes (the cleavage of butadiene by *trans*-but-2-ene) in the presence of this catalyst reached 39% in the best case, but mostly did not exceed 10%. The selectivity in relation to the desired products was 46–100%. The reaction is complicated by the oligomerisation of the dienes in the presence of a tungsten catalyst (the amount of dimers in individual experiments reached 32%).

An interesting observation of the formation of cyclohexadiene (instead of the expected hexatriene) was made in the disproportionation of buta-1,3-diene:

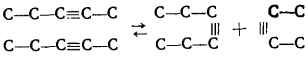


The disproportionation of dienes together with mono-olefins (a process similar to ethenolysis) makes it possible to obtain with a high degree of selectivity a new mono-olefin and a diene. For example, ethylene and 4-methylpenta-1,3-diene was obtained with 100% selectivity from buta-1,3-diene and isobutene:



Thus the disproportionation of dienes opens up vast possibilities both for preparative synthesis and for the industrial manufacture of valuable diene hydrocarbons of different structures.

The wide variety of disproportionation reactions of unsaturated hydrocarbons is also shown by the fact that these reactions are undergone by alkynes[15]. The formation of homologues was noted in many catalytic and thermal reactions of alkynes¶, but the experimental proof of disproportionation was obtained only recently for pent-2-yne[15]. The catalyst was tungsten oxide on silica gel. When the reaction was performed in a stream of cyclohexane at 350°C and at atmospheric pressure, pent-2-yne was converted with an overall yield of 44% into but-2-yne and hex-3-yne (molar ratio 1–1.2) and also a polymer. The selectivity with respect to the alkynes is 53%.



The first experiments on the disproportionation of alkynes left no doubt that this reaction, like that in the series of alkenes, constitutes a new means for the synthesis of a wide variety of acetylene homologues.

Summarising the applications of heterogeneous disproportionation catalysts, one must emphasise some of their advantages, such as relatively ready availability, the possibility of employment for a wide range of olefins (C_3–C_{40}, regardless of the position of the multiple bond and the degree of chain branching), and also a very favourable olefin: catalyst ratio (between 1000 : 1 and 1 : 1).

At the same time mention must be made of some important disadvantages of heterogeneous disproportionation. These include in the first place inadequate process selectivity. This applies in particular to higher olefins, the disproportionation products of which must be regarded as the result of two competing processes: double bond migration, and disproportionation. The reaction is apparently sufficiently selective only for the special case of the disproportionation of propene to ethylene and straight-chain butenes.

In addition, in the presence of heterogeneous catalysts the disproportionation usually takes place at elevated temperatures and pressures, which gives rise to certain disadvantages in the technological formulation of the process. Finally, another negative feature is the lack of continuity in the disproportionation process using heterogeneous catalysts owing to the comparatively extensive coke deposition on them during operation (up to 20%).

III. HOMOGENEOUS DISPROPORTIONATION OF OLEFINS

The disproportionation of olefinic hydrocarbons is one of the catalytic processes for which homogeneous catalysis by complex compounds has only just begun to be employed. Nevertheless, the few available data[17–24] on this problem indicate a wide scope of homogeneous disproportionations, primarily in the solution of applied problems involving the synthesis of various olefins. At the same time, the use of homogeneous catalysts makes it possible to obtain more profound information about the reaction mechanism.

The homogeneous catalysts at present available, which are capable of catalysing the disproportionation of olefins, are largely based on tungsten and molybdenum complexes.

The study of homogeneous disproportionation was begun by Calderon and coworkers[17–19], who reported the disproportionation of olefins in the presence of a new catalytic system (for this reaction), consisting of tungsten hexachloride, ethylaluminium dichloride and ethyl alcohol, using benzene as the solvent. A much less active catalyst was obtained without ethyl alcohol. None of the systems component alone is an active catalyst of the disproportionation or migration of the C=C bond (under the process conditions). The aluminium : tungsten ratio can be varied within wide limits, but best results were obtained for a 4 : 1 ratio. The $WCl_6 + C_2H_5AlCl_2 + C_2H_5OH$ catalytic system proved very effective in the disproportionation of C_4 and higher olefins with a non-terminal double bond. The reaction was achieved at room temperature and atmospheric pressure; equilibrium was established extremely rapidly (in seconds).

The selectivity of the homogeneous disproportionation proved to be very high. Thus in the case of pent-2-ene, but-2-ene, and hex-3-ene, it reached 99.6%.

A relative disadvantage of the $WCl_6 + C_2H_5AlCl_2 + C_2H_5OH$ catalytic system is slight oligomerisation of olefins, which was found to depend on the position of the double bond in the alkene and decreased in the sequence but-2-ene > alk-2-ene > alk-3-ene > alk-6-ene. The solvent (benzene) was alkylated to a very slight extent. There was also some loss of activity of the catalyst with time.

¶The disproportionation of acetylene has been postulated in its photolysis[83].

The binary catalytic system comprising tungsten hexachloride and n-butyl-lithium is free from all these disadvantages [20], the second component playing the role of a reducing and alkylating agent for WCl_6. Neither tungsten hexachloride nor n-butyl-lithium gives rise separately to olefin reactions, i.e. any anionic (due to C_4H_9Li) or cationic (due to WCl_6) processes can be completely ruled out. The new homogeneous catalyst proved to more be selective. For example, pent-2-ene was converted with 100% selectivity into but-2-ene and hex-3-ene regardless of the degree of conversion.

However, in contrast to the preceding homogeneous system, where the olefin : WCl_6 ratio could reach 10 000, the catalyst with n-butyl-lithium was sufficiently effective only for olefin : WCl_6 ratios not exceeding 100 (the optimum ratio was 50).

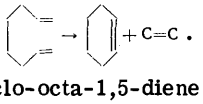
The dependence of catalyst activity on the Li/W ratio has not so far been explained. It was found that the system catalyses effectively the disproportionation of pent-2-ene only for a 2 : 1 ratio of these metals.

The attempts to replace the n-butyl group by isomeric groups were unsuccessful. The conversion of pent-2-ene decreased in the series n-butyl > s-butyl > t-butyl and after 15 min of reaction, amounted to 15, 4, and 0% respectively.

Recently reports have been published [21-24] about yet another type of homogeneous catalytic system for the disproportionation of olefins—the nitrosyl complexes $L_2Cl_2(NO)_2M$ (where M = Mo or W and L = Ph_3P, C_5H_5N, PH_3PO, and others) treated with alkylaluminium chlorides in chlorobenzene. Like the previous homogeneous catalysts, these systems are effective at a low temperature (0–50°C).

The activity of the nitrosyl catalytic complex depends on the nature of the metal and the ligand [21,23]. Tungsten-containing catalysts are less active than the analogous molybdenum compounds. The $(C_5H_5N)_2Cl_2(NO)_2Mo$ complexes showed the highest selectivity. In addition to the disproportionation reaction the systems including ethylaluminium dichloride as a co-catalyst catalyse also the isomerisation reaction, which greatly reduces the process selectivity. The most active catalyst was obtained with methylaluminium sesquichloride.

It should be noted that the effectiveness of the homogeneous disproportionation in the presence of nitrosyl complexes is as a whole much lower than in the presence of the systems with tungsten hexachloride indicated above. However, nitrosyl-containing catalysts are very effective in the disproportionation of $\alpha\omega$-dienes and cyclic olefins with ethylene [23]. Thus octa-1,7-diene undergoes intramolecular disproportionation with formation of cyclohexene as the main product:



The ethenolysis of cyclo-octa-1,5-diene leads to the formation of deca-1,5,9-triene.

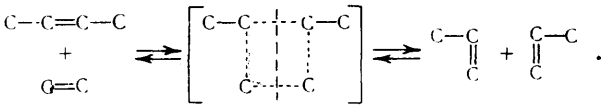
The kinetics of the homogeneous disproportionation of pent-2-ene were investigated, using the nitrosyl complexes described above [24]. The order of the reaction, which is unity with respect to the catalyst and variable with respect to the olefin, was determined: at a low olefin concentration the order is closer to 2, while at very high concentrations it approaches unity. The activation energy was found to be 6.6 kcal $mole^{-1}$.

Comparison of the results of applying catalytic systems of various types in the disproportionation of olefins makes it possible to define clearly the advantages of homogeneous over heterogeneous catalysts. The most important of these are milder process conditions combined with a high efficiency, selectivity, and stereospecificity (this feature is discussed in the last section of the review) and relative simplicity of action, which makes it possible to establish the most significant features of the kinetics and mechanism of the reaction.

Hence the urgent necessity to continue the search for complex catalytic systems for homogeneous disproportionation of olefins is quite evident.

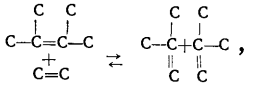
IV. MECHANISM OF DISPROPORTIONATION

The mechanism of both heterogeneous and homogeneous disproportionations of olefins is essentially based on the concept of the coordination of unsaturated ligands (olefins) with transition metals. The first considerations in relation to the mechanism of the reaction concern its occurrence in the presence of heterogeneous catalysts. Banks and Bailey [5] and then Bradshaw and coworkers [6] put forward the hypothesis that the intermediate stage in the disproportionation of olefins involves the formation of a four-membered ring—"quasicyclobutane". The reaction carried out by Bradshaw and coworkers [6], which is the reverse of the disproportionation of propene, i.e. the ethenolysis of but-2-ene ($CoO–MoO_3$ catalyst), may be regarded as confirming to some extent this hypothesis. They suggested, in accordance with the mechanism involving the formation of quasicyclobutane, that the only reaction product is propene:



A further development of the hypotheses concerning the disproportionation mechanism may be found in the work of Mol and coworkers [84,85], who suggested the formation of 1,2-dimethylcyclobutadiene (in the case of propene) as an intermediate. They also believe that the intermediate is formed as a result of the adsorption of two olefin molecules on the catalyst surface.

Quite recently Crain [7] questioned Mol's hypothesis of the formation of cyclobutadiene π-bonds by the transfer of four hydrogen atoms from two olefin molecules to the catalyst surface. He based his criticism on the ethenolysis of 2,3-dimethylbut-2-ene,

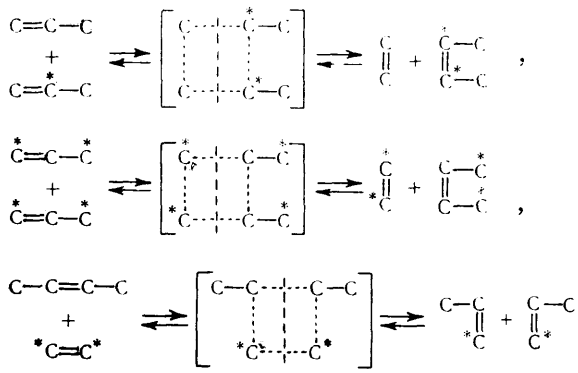


the product of which is isobutene, whereas according to Mol's hypothesis of the migration of hydrogen atoms to the catalyst the process should lead to methylbutenes, propene, and straight-chain butenes. Nevertheless, no traces of these substances were found in the ethenolysis products.

Important evidence in favour of the disproportionation mechanism involving the formation of an intermediate four-membered surface ring was provided by the study of the reaction using radioactive olefins [75,85-88].

In the disproportionation of [2-^{14}C] propene in the presence of Re_2O_7/Al_2O_3 [83] or in the presence of alumina alone [75], it was found that among the products only the straight-chain butenes exhibit specific radioactivity and that it is twice as high as for the initial propene. In the

case of propene with the extreme carbon atoms labelled, i.e. [1,3-^{14}C]propene, both reaction products, i.e. ethylene and straight-chain butenes, proved to be radioactive. Moreover, in the ethenolysis of but-2-ene using radioactive ethylene, propene containing radioactive carbon was isolated. The result described could have been obtained for the following disproportionation mechanism:

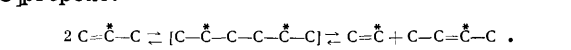


The mechanism of the disproportionation of propene in the presence of a cobalt–molybdenum catalyst was also investigated with the aid of radioactive carbon, attention being concentrated on the isomerisation reaction [87,88]. The results of these experiments confirmed the validity of the four-centre mechanism. Clark and Cook [88] note that at low temperatures (60°C) in the reaction involving [1-^{14}C]propene radioactivity was detected only in ethylene; [2-^{14}C]propene gave rise to radioactive butene. However, at an elevated temperature (100–160°C) the disproportionation of [1-^{14}C]propene yields two radioactive products —ethylene and butene, which the authors believe can be explained by the isomerisation of [1-^{14}C]propene to [3-^{14}C]propene. The apparent activation energy for disproportionation is 7.7 kcal mole^{-1} and for isomerisation 17.3 kcal mole^{-1}. On the other hand, the authors do not rule out the possibility of the formation at high temperatures of two adsorbed π-allyl complexes in the disproportionation of which the radioactive atom will enter ethylene and butene with equal probability.

Banks and Bailey [86] postulated that the four-centre mechanism is common to various reactions of olefins (disproportionation, isomerisation, polymerisation, etc.), the reaction pathway depending on the ability of the catalyst to promote the migration of hydrogen atoms. In particular, disproportionation takes place when olefin molecules are adsorbed with formation of a four-centre complex, the desorption involving the dissociation of two opposite bonds without the migration of hydrogen.

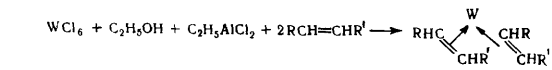
The results of numerous experiments on the disproportionation of mono-olefins with a wide variety of structures [6–8] and also diolefins [14] and acetylenes [15] agree satisfactorily with the hypothesis of the formation of an intermediate surface cyclobutane and constitute an additional argument in favour of the "quasicyclobutane" mechanism.

Thus it is possible to exclude the "linear" mechanism of the disproportionation of olefins [90] according to which radioactive ethylene and but-1-ene should be formed from [2-^{14}C]propene:



Homogeneous disproportionation yields much more complete information about the reaction mechanism. In their discussion of the mechanism of homogeneous disproportionation, Calderon and coworkers [17–19] also began with the hypothesis of an intermediate four-membered cyclic compound as the transition state and the possibility of its formation was considered wholly using the hypothesis of the coordination of olefins to transition metals. According to the concept of these authors, the disproportionation of olefins consists of three consecutive stages; the formation of a bisolefin–metal complex, transalkylidenation, and finally exchange of the olefins in the complex.

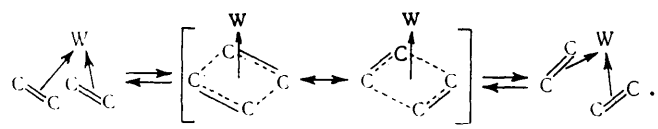
The first reaction stage, i.e. the formation of the bisolefin complex with tungsten, probably includes as an initial stage the reaction of tungsten(VI) with $C_2H_5AlCl_2$ in the presence of the free olefin, which leads to the reduction of tungsten(VI) to tungsten(IV):



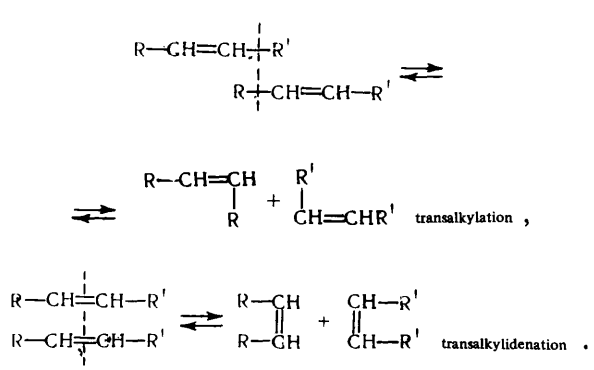
(The capacity of organoaluminium compounds to reduce transition metal halides is well known.)

Next tungsten(IV) is coordinated to two molecules of the olefinic ligand in the *cis*-configuration with formation of a bisolefin complex. The olefin bonds in the latter may be delocalised, as in the analogous structure of norbornadienetungsten tetracarbonyl. It is suggested that two olefin molecules form a four-membered ring—the square base of a tetragonal pyramid with the tungsten atom at the apex. The positions of the remaining ligands have not so far been determined. Nor is the role of ethanol in the catalytic reaction clear.

The next stage is transalkylidenation, consisting in the dissociation of the double bonds weakened by the coordination of the olefin to the metal [tungsten(IV)] and the formation of new multiple bonds:

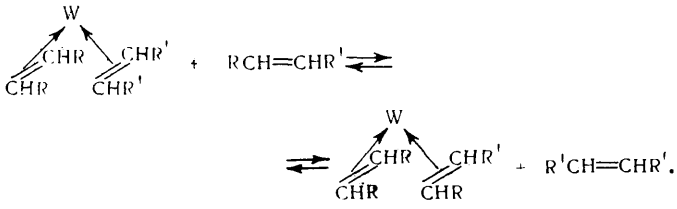


The transalkyledination mechanism, i.e. the exchange of alkylidene and not alkyl groups in disproportionation, was proved experimentally in experiments with deuterated olefins [18,19]:



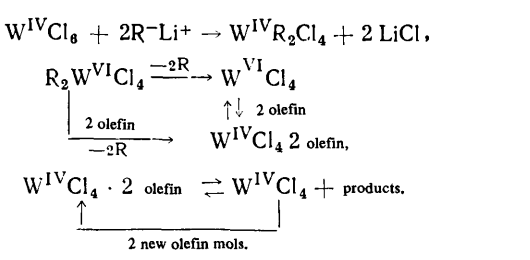
The isotope composition of the products agrees only with the four-centre mechanism.

Finally, the last reaction step—the exchange of the olefinic ligands in the coordination complex—alternates with the preceding stage—transalkylidenation:



The high rate of homogeneous disproportionation can be explained only by a very high rate of the last stage, i.e. the exchange of olefinic ligands. Examples of fast exchange reactions involving certain complexes of olefins with metals are known [91,92]. Thus the replacement of ethylene in Zeise's salt $K[(CH_2{=}CH_2)PICl_3].H_2O$ by other olefinic ligands is very rapid [91,93].

The work of Wang and Menapace[20] on a catalytic system comprising tungsten hexachloride and n-butyl-lithium constitutes further confirmation of the role of coordination interaction in the olefin disproportionation mechanism. Their reaction mechanism includes the substitution of two chlorine atoms in tungsten hexachloride by two alkyl groups, the subsequent mono- or bi-molecular reduction of tungsten(VI) to tungsten(IV), and the coordination of the latter to two pent-2-ene molecules:



The formation of the reaction products from the intermediate coordination complex $W^{IV}Cl_4.2$olefin and the regeneration of the catalyst can be explained using the concepts of Calderon and coworkers [18,19].

Some information concerning the reaction mechanism can be obtained from the analysis of the results reported recently by Kotari and Tatsuma [92], who found that the WCl_6–ethylaluminium dichloride catalytic system can catalyse both alkylation and disproportionation reactions depending on the way in which the process is carried out. If the catalyst is prepared first (in toluene) and then the olefin (pent-2-ene) is added, toluene is rapidly alkylated. When pent-2-ene is added to toluene, then tungsten hexachloride, and finally ethylaluminium dichloride, disproportion mainly takes place. The authors suggested that the catalytically active complex contains reduced tungsten [tungsten(IV)] coordinated to the solvent and aluminium via chlorine bridges. The "quasicyclobutane–tungsten" complex can be converted into a catalytically inactive state by the action of toluene.

It is noteworthy that recently data have been published showing the possibility that homogeneous disproportionation can be interpreted in terms of a non-concerted mechanism including an oxidative addition stage. Thus in a study of the valence isomerisation of cubane catalysed by rhodium compounds, Cassar et al. [94] concluded that the reaction proceeds via a non-concerted oxidative addition mechanism and suggested that the mechanism for a number of reactions, including the disproportionation reaction, might be revised appropriately.

V. STEREOCHEMICAL CHARACTERISTICS OF THE REACTION

The stereochemistry of heterogeneous disproportionation has been hardly investigated; some observations concerning the relative amounts of the *trans*- and *cis*-forms of the reaction products were made only in the disproportionation of C_3–C_5 olefins in the presence of a molybdenum oxide catalyst [5]. Moreover, in a few studies the amounts of *cis*- and *trans*-isomers were fixed. It is therefore at present impossible to arrive at any conclusion concerning the stereoselectivity of heterogeneous disproportionation catalysts.

The stereospecificity of homogeneous catalytic systems is much more pronounced. The stereochemistry of homogeneous disproportionation was investigated using complex catalysts based on tungsten [19,20] and also nitrosyl complexes of molybdenum [22].

Initially, it was found [19] that in the disproportionation of pentene and hexenes (with an internal double bond) in the presence of the WCl_6–$C_2H_5AlCl_2$ + C_2H_5OH catalytic system *trans*-*cis*-products are formed in the proportions predicted by thermodynamics. The final proportions of the isomers are then independent of the *trans*/*cis* ratio in the initial olefins.

The stereochemistry of homogeneous disproportionation was investigated in greater detail [20] in the presence of the WCl_6 + C_4H_9Li complex catalyst, using pure *cis*- and *trans*-isomers of pent-2-ene and also their mixture as the initial olefins. The results of this investigation differ from those of the previous studies. It was found that the ratio of the isomers in the reaction products depends to some extent on the *trans*–*cis* distribution in the initial olefins. The latter factor also determines the degree of conversion of the olefins. The *trans*-isomer reacts much more slowly than the *cis*-isomer or the mixture of the two isomers.

The stereospecificity of the catalyst is fairly high; for example, in the disproportionation of a mixture consisting of 46% of *trans*- and 54% of *cis*-isomers of pent-2-ene the final *trans*/*cis* ratio for but-2-ene was 4.2, which corresponds to 81% of the *trans*-form.

All these findings were fairly convincingly explained on the hypothesis of the formation of an intermediate bisolefin complex [20]. Thus the lower reactivity of *trans*-pent-2-ene compared with the *cis*-isomer is evidently due to the steric hindrance arising in the coordination of *trans*-olefins to the metal.

The discrepancy between the results obtained in the presence of different catalysts for the dependence of the *trans*/*cis* ratio in the reaction products on the stereochemical composition of the initial olefin can probably be explained by additional stereoisomerisation, which may occur owing to cationic aluminium-containing fragments.

Among homogeneous catalysts, nitrosylmolybdenum complexes $(C_5H_5N)_2Mo(NO)_2Cl_2.C_2H_5AlCl_2$ showed the highest stereoselectivity, as demonstrated by the conversion of pent-2-ene into but-2-ene and hex-3-ene [22]. The ratios of the *trans*- and *cis*-isomers of all three olefins reached the equilibrium values regardless of the isomeric nature of the initial pent-2-ene. However, it was found that in the early stages of the reaction the ratio of the isomers is appreciably determined by that in the initial olefin.

Interesting correlations were established between the total concentration of *cis*-olefins in the reaction mixture and the degree of conversion. The rate of disproportionation and the rate of stereoisomerisation were found to

decrease simultaneously, which is apparently evidence of a close relation between these processes and of their occurrence in the presence of the same catalyst.

To account for the above finding, the bisolefin–metal model for the intermediate complex has been successfully employed[22].

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It is not difficult to predict that in the near future new homogeneous systems catalysing the disproportionation of unsaturated hydrocarbons will be found. One can also expect that homogeneous catalysis will make it possible to solve many problems of the practical application of the reaction. The elucidation of the mechanism of the action of homogeneous disproportionation catalysts will promote the application of theoretical concepts in the chemistry of complex compounds to catalytic problems.

At the same time one should expect further advances in the selection and modification of heterogeneous catalysts for the disproportionation of olefins.

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Polycondensation Reactions of Fluorinated Organic Compounds

R.M.Gitina, E.L.Zaitseva, and A.Ya.Yakubovich (deceased)

The review deals with the principal advances in the synthesis and investigation of the properties of polycondensation of fluoro-polymers. In many cases the properties of the fluoro-polymers have been compared with those of their non-fluorinated analogues. The applications of the polymers are also described briefly.
The bibliography includes 138 references.

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I. INTRODUCTION

The study of organofluorine polymers and low-molecular-weight compounds of this class began to develop comparatively recently—during the 1940's. The scope of the chemistry of fluorinated macromolecular compounds was of course limited mainly by the relatively low level of development of the chemistry of fluorinated low-molecular-weight compounds. This was responsible for the fact that until recently (until the 1950's) the principal methods for the synthesis of fluoro-polymers consisted in the polymerisation of the relatively readily available fluorinated olefins, which yielded polyperfluoroalkylenes. Polymerisation fluoro-polymers, particularly polytetrafluoroethylene (Teflon), which is the most important member of this class, have found a firm place among modern polymeric materials employed under severe operating conditions.

By virtue of the considerable advances in organofluorine chemistry in recent years, many aspects of this field, which were either impossible or difficult to achieve, have become more or less commonplace, in particular methods for the synthesis and the study of the properties or organic perfluoro-compounds and polyfluorinated compounds with a wide variety of functional groups have been developed on a large scale [1]. This led to the expansion of studies on the synthesis and properties of fluorinated polymers obtained by methods for the polycondensation of bi- and poly-functional monomers. The application of the polycondensation methods of synthesis to fluoro-polymers led to a much greater variety of the structures of macromolecules and thus to the development of new essential materials.

Much attention has been devoted to problems of the synthesis of polymerisation fluoro-polymers, their properties, and applications; the present review gives the first systematic account of polycondensation fluoro-polymers. It covers the original literature (including patents) up to the end of 1969 and deals with fundamental work on the synthesis and properties of polycondensation fluoro-polymers containing fluorine atoms in the main macromolecular chain and those obtained on the basis of bifunctional derivatives of 2,2-diphenylperfluoropropane.

II. FLUORINE-CONTAINING POLYESTERS AND POLYTHIOESTERS

Fluorine-containing polyethers are mainly obtained by the polymerisation of epoxyfluoroalkanes. In contrast, polyesters are synthesised by the polycondensation method.

The first fluorine-containing aliphatic polyesters were described in 1952. [2] At the present time fluorine-containing aliphatic, alkylene, aromatic, and fully aromatic polyesters are known. Depending on which component contains fluorine, polyesters can be divided into two types: (1) polyesters from fluorinated dicarboxylic acids and non-fluorinated diols; (2) polyesters from fluorinated dicarboxylic acids and fluorinated diols; (3) polyesters from non-fluorinated dicarboxylic acids and fluorinated diols. Table 1 lists the fluorine-containing polyesters described in the literature and some of their properties.

Aliphatic polyesters of the first type were obtained by the direct esterification of glycols by perfluoroalkanedicarboxylic acids [2,3]:

$$HO(CH_2)_m OH + HOOC(CF_2)_p COOH \xrightarrow{-H_2O} [-O(CH_2)_m OCO(CF_2)_p CO-]_n,$$

and also by the reaction of the silver salts of these acids with $\alpha\omega$-di-iodoalkanes [3]. The polyesters synthesised by the second method have lower viscosities than those obtained by direct esterification.

Data have also been published on the synthesis of fluorine-containing polythioesters by the reaction of pentane-1,5-dithiol and perfluoroglutaric acid dianhydride [4] and also by the reaction of hexane-1,6-dithiol with polyfluorochlorohexanedicarboxylic acid [5]. Aliphatic polyesters of the second type can be obtained by the reaction with tetrahydroperfluoroalkane-$\alpha\omega$-diols of both perfluoroalkanedicarboxylic acids in the presence of zinc chloride as a catalyst [6,7] and their dianhydrides [8]; however, these polyesters have a low molecular weight. Polyesters with a high molecular weight can be obtained using acid dichlorides [6,7], since fluorinated diols are acidic compounds and are esterified with difficulty.

It is noteworthy that polyesters obtained from perfluoroalkanedicarboxylic acids are hydrolysed much faster than their non-fluorinated analogues [3,8] and therefore they have not found practical applications [7]. The enhanced

Table 1. Fluorine-containing polyesters and polythioesters.

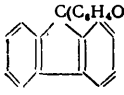
Initial components		Certain properties of polymers	References
glycols, iodides, and thioglycols	acids and their derivatives		
$(CH_2)_2(OH)_2$	$(CF_2)_4(COOH)_2$	Waxy substance T_f = 129–133°C; insol. in hydrocarbons and usual organic solvents	2
$(CH_2)_4(OH)_2$	$(CF_2)_3(COOH)_2$	Viscous oil	3
$(CH_2)_3I_2$	$(CF_2)_3(COOAg)_2$	ditto	3
$(CH_2)_3I_2$	$(CF_2)_3(COOAg)_2$	,,	3
$(CH_2)_2(OH)_2$	$C_6F_4(COOCH_3\text{-}p)_2$		35
$(CH_2)_5(SH)_2$	$CF_2(CF_2CO)_2O$	Waxy substance, insol. in usual organic solvents	4
$(CH_2)_6(SH)_2$	$(CF_2CFCl)_4(COOH)_2$	Solid substance, insol. in ααα-trifluorotoluene	5
$C(CH_3)_2(C_6H_4OH\text{-}p)_2$	$C(CF_3)_2(C_6H_4COCl\text{-}p)_2$	η_{inh} = 0.4, (Ref.8) T_{soft} = 290°C; polymer soluble in many organic solvents; strong sheet formed from solutions	27, 28
	$C(CF_3)_2(C_6H_4COCl\text{-}p)_2$	η_{inh} = 0.66, T_{soft} = 340°C; polymer soluble in many organic solvents; strong sheets formed from solutions	27, 28
$C(CH_3)_2(C_6H_4OH\text{-}p)_2$	$i\text{-}C_6F_4(COCl)_2$	$\eta_{inh} \simeq 0.1$	36
$(CF_2)_3(CH_2OH)_2$	$(CF_2)_3(COOH)_2$	$M \simeq 8000\text{–}9000$, T_{degr} = 380°C	6,7
$(CF_2)_3(CH_2OH)_2$	$(CF_2)_3(COCl)_2$		7,18
$(CF_2)_3(CH_2OH)_2$	$CF_2(CF_2CO)_2O$		8
$(CF_2)_3(CH_2OH)_2$	$(CF_2)_4(COOH)_2$	Viscous liquid, slowly crystallising	6,7
$(CF_2)_3(CH_2OH)_2$	$(CF_2)_4(COCl)_2$	M = 6570, $T_{brittle}$ = –55°C, T_f = 35°C	6,7
$(CF_2)_3(CH_2OH)_2$	$C_7F_{15}CF(CF_2COCl)_2$	M = 9920	7
$(CF_2)_3(CH_2OH)_2$	$C_3F_7CH(CH_2COCl)_2$	Viscous liquid, M = 7200, $T_{brittle}$ = –25°–30°C	6,7
$(CF_2)_3(CH_2OH)_2$	$S[CH(C_3F_7)CH_2COCl]_2$	M = 7480	7
$(CF_2)_3(CH_2OH)_2$	$(CF_2)_3(CH_2OCH_2COCl)_2$	M = 5360	7
$(CF_2)_3(CH_2OH)_2$	$(CF_2)_3(C_6H_4COCl\text{-}m)_2$	T_g = 16°C, T_{soft} = 20°C, T_f = 147°C	33
$(CF_2)_5(CH_2OH)_2$	$(CF_2)_5(C_6H_4COCl\text{-}m)_2$	T_g = 16°C, T_{soft} = 20°C, T_f = 125°C	33
$(CF_2)_4(CH_2OH)_2$	$(CF_2)_3(COOH)_2$		6,7
$(CF_2)_4(CH_2OH)_2$	$(CF_2)_3(COCl)_2$	$M \simeq 8800\text{–}9900$	7
$(CF_2)_4(CH_2OH)_2$	$CF_2(CF_2CO)_2O$		8
$(CF_2)_4(CH_2OH)_2$	$(CF_2)_4(COCl)_2$	Waxy substances, M = 5260, T_f = 65–70°C	6,7
$(CF_2)_4(CH_2OH)_2$	$C_7F_{15}CF(CF_2COCl)_2$	M = 10400	7
$(CF_2)_4(CH_2OH)_2$	$C_3F_7CH(CH_2COCl)_2$	M = 9940	7
$(CF_2)_4(CH_2OH)_2$	$S(CH(C_3F_7)CH_2COCl]_2$	M = 7400	7
$(CF_2)_4(CH_2OH)_2$	$(CF_2)_3(CH_2OCH_2COCl)_2$	M = 6850	7
$(CF_2)_3(C_6H_4OH\text{-}m)_2$	$(CF_2)_3(C_6H_4COCl\text{-}m)_2$	T_g = 46°C	33
$C(CF_3)_2(C_6H_4OH\text{-}p)_2$	$(CF_2)_4(COCl)_2$	η_{log} = 0.30, T_{soft} = 120°C, sol. in tetrachloroethane, amorph.	26
$C(CF_3)_2(C_6H_4OH\text{-}p)_2$	$(CF_2)_6(COCl)_2$	η_{log} = 0.40, T_{soft} = 80°C, sol. in tetrachloroethane	26

Table 1 cont'd

Initial components: glycols, iodides, and thioglycols	Initial components: acids and their derivatives	Certain properties of polymers	References
$C(CF_3)_2(C_6H_4OH\text{-}p)_2$	$C(CF_3)_2(C_6H_4COCl\text{-}p)_2$	$\eta_{inh} = 0.5$, $T_{soft} = 280°C$; polymer sol. in many organic solvents, strong sheets formed from solutions	27, 28
$C_6H_5C(CF_3)(C_6H_4OH\text{-}p)_2$	$C(CF_3)_2(C_6H_4COCl\text{-}p)_2$	$\eta_{inh} = 0.72$, $T_{soft} = 300°C$, strong sheets formed from solution	27, 28
$(C_6F_4OH\text{-}p)_2$	$m\text{-}C_6F_4(COCl)_2$	$T_{soft} = 300°C$, $T_f > 400°C$	34
$(C_6F_4OH\text{-}p)_2$	$p\text{-}C_6F_4(COCl)_2$		34
$(C_6F_4OH\text{-}p)_2$	$m\text{-}C_6F_4(OCOCl)_2$		36
$C_6F_4(OH\text{-}m)_2$	$m\text{-}C_6F_4(OCOCl)_2$	$\eta_{inh} = 0.04\text{-}0.1$	36
$C_6F_4(OH\text{-}m)_2$	$CO(OC_6H_5)_2$		36
$(CF_2)_3(CH_2OH)_2$	$(CH_2)_3(COCl)_2$	Waxy substance; $M = 6020\text{-}7930$, $T_{brittle} = -50\text{-}-55°C$, $T_f = 40°C$	6, 10
$(CF_2)_3(CH_2OH)_2$	$(CH_2)_4(COOH)_2$	Viscous liquid, crystallising slowly; $M = 9000$	6
$(CF_2)_3(CH_2OH)_2$	$(CH_2)_4(COCl)_2$	Rubberlike substance, crystallising slowly; $M = 20000\text{-}25000$, $T_{brittle} = 65°C$, $T_g = 57°C$, $T_f = 30°C$, $T_{decomp} = 380°C$ (helium)	6, 10, 12, 14, 16, 18
$(CF_2)_3(CH_2OH)_2$	$(CH_2)_6(COCl)_2$	$M = 7480$, $T_{brittle} = -75°C$, $T_f = 20\text{-}26°C$	10
$(CF_2)_3(CH_2OH)_2$	$(CH_2)_7(COCl)_2$	$M = 12000$, $T_f = 30°C$, $T_{brittle} = -48\text{-}65°C$	10
$(CF_2)_3(CH_2OH)_2$	$(CH_2)_8(COCl)_2$	$M = 11000$, $T_f = 30°C$, $T_{brittle} < -65°C$	10
$(CF_2)_3(CH_2OH)_2$	$(CH_2SCH_2COOH)_2$	Rubberlike substance; $T_{brittle} = -40°C$	6
$(CF_2)_3(CH_2OH)_2$	$(CH_2SCH_2COOC_2H_5)_2$		10
$(CF_2)_3(CH_2OH)_2$	$CH_2(SCH_2COOH)_2$	Waxy substance; $T_f = 55°C$	6
$(CF_2)_3(CH_2OH)_2$	$p\text{-}C_6H_4(COCl)_2$	Solid sol. in acetone, ethyl acetate, and methylene chloride; $T_f = 107°C$	13, 19
$(CF_2)_3(CH_2OH)_2$	$m\text{-}C_6H_4(COCl)_2$	Transparent pale-brown solid; films and fibres formed from the melt; $\eta_{inh} = 0.16$, $T_g = 22°C$, $T_{decomp} = 460\text{-}480°C$ (nitrogen, helium)	12, 18
$(CF_2)_3(CH_2OH)_2$	$1,3,5\text{-}(COOH)_2(n\text{-}C_5H_{11}O)C_6H_3$	Dark solid partly sol. in DMFA	20
$(CF_2)_3(CH_2OH)_2$	$1,3,5\text{-}(COCl)_2(n\text{-}C_5H_{11}O)C_6H_3$	Dark rubberlike substance sol. in DMFA; $\eta_{inh} = 0.18$, $T_{decomp} = 440°C$, $T_g = -30°C$	20
$(CF_2)_3(CH_2OH)_2$	$1,3,5\text{-}(COOC_2H_5)_2(n\text{-}C_5H_{11}O)C_6H_3$	$\eta_{inh} = 0.28$, $T_{decomp} = 445°C$ (nitrogen)	20
$(CF_2)_3(CH_2OH)_2$	$1,3,4\text{-}(COOCH_3)_2(n\text{-}C_5H_{11}O)C_6H_3$	Dark rubberlike substance; $\eta_{inh} = 0.25$, $T_{decomp} = 410°C$, $T_g = 9°C$	20

Table 1 cont'd

Initial components: glycols, iodides, and thioglycols	Initial components: acids and their derivatives	Certain properties of polymers	References
$(CF_2)_3(CH_2OH)_2$	1,3,2-$(COOCH_3)_2$ $(n\text{-}C_5H_{11}O)C_6H_2$	Dark rubberlike substance; $\eta_{inh} = 0.12$, $T_{decomp} = 400°C$, $T_g = 17°C$	20
$(CF_2)_3(CH_2OH)_2$	$o\text{-}C_6H_4(COCl)_2$	$T_{decomp} = 480°C$ (helium); sheets and fibres formed from the melt	12, 18
$(CF_2)_3(CH_2OH)_2$	$o\text{-}C_6H_4(COCl)_2$	$T_{decomp} = 480°C$ (helium)	18
$(CF_2)_3(CH_2OH)_2$	$(C_6H_4COCl\text{-}o)_2$	$T_g = 45°C$, $T_{soft} = 50°C$, $T_f = 145°C$	33
$(CF_2)_3(CH_2OH)_2$	$O(C_6H_4COCl\text{-}p)_2$	$T_{decomp} = 500°-520°C$ (helium); sheets formed from the melt	18
$(CF_2)_3(CH_2OH)_2$	$O(C_6H_4COCl\text{-}m)_2$	$T_g = 20°C$, $T_{soft} = 28°C$, $T_g = 115°C$	33
$(CF_2)_3(CH_2OH)_2$	$(CH_2)_5(OC_6H_4COCl)_2$	$T_{decomp} = 480°C$ (helium)	18
$(CF_2)_4(CH_2OH)_2$	$(CH_2)_3(COCl)_2$	Waxy substance, $M = 6600$–8950, $T_{brittle} = -50$–$55°C$, $T_f = 40°C$	6,10
$(CF_2)_4(CH_2OH)_2$	$(CH_2)_4(COCl)_2$	Waxy substance; $M = 18300$–24000, $T_f = 60$–$70°C$	6,10
$(CF_2)_4(CH_2OH)_2$	$(CH_2)_6(COCl)_2$	$M = 8800$, $T_f = 58$–$61°C$	10
$(CF_2)_4(CH_2OH)_2$	$(CH_2)_7(COCl)_2$	$M = 13000$, $T_f = 47$–$50°C$	10
$(CF_2)_4(CH_2OH)_2$	$(CH_2)_8(COCl)_2$	$M = 65800$, $T_f = 55$–$60°C$	10
$(CF_2)_4(CH_2OH)_2$	$C_3H_7CH(CH_2COCl)_2$	Viscous liquid; $M = 8770$, $T_{brittle} = -25°C$	6
$(CF_2)_4(CH_2OH)_2$	$(CH_2SCH_2COOH)_2$	Rubberlike substance; $T_{brittle} = -38°C$	6
$(CF_2)_4(CH_2OH)_2$	$CH_2(SCH_2COOH)_2$	Waxy substance; $T_f = 70$–$75°C$	6
$m\text{-}(CF_2)_5(CH_2OH)_2$	$m\text{-}C_6H_4(COOH)_2$		19
$(CF_2)_5(CH_2OH)_2$	$m\text{-}C_6H_4(COOCH_3)_2$		19
$O(CF_2CF_2CH_2OH)_2$	$(CH_2)_4(COCl)_2$	Viscous liquid $M = 16700$, $T_{brittle} = -58°C$	11
$C(CF_3)_2(C_6H_4OH\text{-}p)_2$	$p\text{-}C_6H_4(COCl)_2$	$T_{soft} = 340°C$; slightly sol. in chloroform and cresol; cryst.	22, 23, 26
$C(CF_3)_2(C_6H_4OH\text{-}p)_2$	$m\text{-}C_6H_4(COCl)_2$	$\eta_{log} = 0.60$, $T_{soft} = 240°C$; sol. in chloroform and cresol; cryst.; forms strong sheets	23
$C(CF_3)_2(C_6H_4OH\text{-}p)_2$	$(C_6H_4COCl\text{-}p)_2$	$T_{soft} = 400°C$; slightly sol. in chloroform and 3:1 tetrachloroethane–phenol mixt.	25
$(CF_3C(C_6H_5)(C_6H_4OH\text{-}p)_2$	$p\text{-}C_6H_4(COCl)_2$	$\eta_{log} = 0.60$, $T_{soft} = 290°C$; sol. in chloroform and cresol; amorph.; forms strong sheets	23, 26
$(CF_3C(C_6H_5)(C_6H_4OH\text{-}p)_2$	$m\text{-}C_6H_4(COCl)_2$	$\eta_{log} = 0.64$, $T_{soft} = 260°C$; sol. in chloroform and cresol; amorph.; forms strong sheets	23, 26
$(CF_2)_3(CH_2OH)_2$	$COCl_2$	Waxy substance; $\eta_{inh} = 0.30$, $T_f = 58$–$60°C$, $T_{decomp} = 450°C$ (air, helium); cryst.	18, 21
$(CF_2)_3(C_6H_4OH\text{-}m)_2$	$COCl_2$	$T_g = 71°C$	33

Table 1 cont'd

Initial components		Certain properties of polymers	References
glycols, iodides, and thioglycols	acids and their derivatives		
$C(CF_3)_2(C_6H_4OH\text{-}p)_2$	$COCl_2$	$M = 25000$, $T_{soft} = 164°C$	22, 30
$C(CF_3)_2(C_6H_4OH\text{-}p)_2$	$CO(OC_6H_5)_2$	Sol. in acetone	30
$C(CF_3)_2(C_6H_4OH\text{-}p)_2$	$CSCl_2$	$M = 12000$, $T_{soft} = 161°C$, $T_f = 215\text{-}220°C$; sol. in carbon tetrachloride, xylene, methylene chloride, and dichloroethane; forms sheets	31

*Here and henceworth the following abbreviations are employed: sol. = soluble; M = molecular weight; $T_{brittle}$, T_g, T_{soft}, T_{decomp}, and T_f are the embrittlement, glass, softening, and decomposition temperatures and the melting point respectively; cryst. = crystalline; amorph. = amorphous; DMFA = dimethylformamide; DMAA = dimethylacetamide; DMSO = dimethyl sulphoxide.

reactivity of the carboxyl carbon atom in these compounds to nucleophilic attack by water molecules is undoubtedly associated with the marked electron-acceptor influence of the perfluoromethylene chain.

The introduction of methylene groups between the carboxyl carbon atom and the perfluoroalkylene chain of the acidic component stabilises the polyesters with respect to hydrolysis [7].

Mixed polyesters obtained from perfluoroglutaric acid and hexafluoropentanediol, containing 2–5 mole % of non-fluorinated diacids or diols such ethylene glycol or 1,2-di(hydroxymethyl)carborane, were described in a recent patent [9]. These polymers are viscous liquids, and it has been suggested that after vulcanisation they can be employed as chemically stable elastomers.

Aliphatic polyesters of the third type have been investigated in greatest detail [6 10–14]. One of the examples of these polyesters, poly(hexafluoro-1,5-pentylene adipate)

$$[-OCH_2(CF_2)_3CH_2OCO(CH_2)_4CO-]_n,$$

has found industrial application in the manufacture of a special oil- and frost-resistant rubber. Although the thermal stability of the latter is not in fact very high, its capacity to retain elastic properties at fairly low temperatures is of some value. The working temperature range for this rubber is between −50° and 150°C. [15] Its degradation has been investigated [16–18].

In contrast to polyesters of the first and second types, some of the polyesters of the third type considered here, for example poly(hexafluoropentylene adipate), have fairly high molecular weights (about 20000)†. Such polyesters have been obtained by the reaction of fluorinated diols with aliphatic acid dichlorides; on the other hand, esterification with acids or their diethyl esters led only to low-molecular-weight polyesters.

All the aliphatic fluorine-containing polyesters synthesised are viscous liquids and rubber- or wax-like substances, many of which are insoluble in the usual organic solvents. It is suggested that the solubility of the polyesters falls with increasing total content of fluorine atoms in the molecule regardless of whether they are in the main or side chain [6].

A rubber-like vulcanised product based on the polyester from 4-oxa-2,2,3,3,5,5,6,6-octafluoroheptane-1,7-diol and adipic acid dichloride, which can be employed at low temperatures, has been described in an American patent [11]. Its embrittlement temperature is −58°C.

$$[-OCH_2(CF_2)_2O(CF_2)_2CH_2OCO(CH_2)_4CO-]_n.$$

In order to enhance the thermal stability while retaining an adequate flexibility of the macromolecule, polyesters containing aromatic units together with perfluoromethylene groups have been synthesised by the polycondensation of hexafluoropentanediol with derivatives of terephthalic [19], isophthalic [18,20], phthalic [18], and p-pentyloxyisophthalic [20] acids and also di-(p-carboxyphenyl) ether and 1,5-di-(p-carboxyphenoxy)pentane [18]. The polymers described in a British patent [19] have been suggested as thermostable casting resins and varnishes.

The possible mechanisms of the degradation of fluorine-containing polyesters have been discussed [18].

Mixed aromatic polyperfluoroalkylene esters, obtained by the joint polycondensation of hexafluoropentanediol with the dichlorides of isophthalic [12] and terephthalic acids [13], have also been described. It has been shown [12] that, following the introduction of 50 mole % of isophthaloyl units into the poly(hexafluoropentylene adipate) chain, the glass temperature of the polymer increases from −57° to −31°C and the rate of crystallisation falls appreciably. The introduction into the polymer chain of up to 30 mole % of terephthaloyl units hardly increases the glass temperature of the polymer (−62° and −60°C for the homopolymer and the copolymer), but the thermal stability increases slightly: the weight losses in a vacuum over a period of

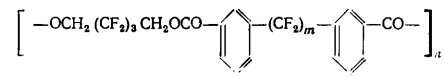
†The molecular weight was determined by measuring the viscosity of the melt by Flory's method and the characteristic constants of the equation relating the viscosity of the melts to the molecular weight of the polymer were found by titrating the terminal groups [6]. Subsequently the viscosities of the solutions of the polymers in chloroform were employed for this purpose [12]. The light-scattering method and measurements of the viscosity of dilute solutions of the polymer have also been employed [14] to determine the molecular weight.

2 h at 250°C are 32.6 and 26.65% for the homopolymer and the copolymer respectively[13].

The polycarbonates obtained by the treatment with phosgene of a mixture of hexafluoropentanediol (80 to 95 mole %) and 2,2-di-(*p*-hydroxyphenyl)propane (20 to 5 mole %) have useful physical and chemical characteristics and are more readily worked into sheets and fibres than the corresponding non-fluorinated analogues[21].

In the 1960's hexafluoro-2,2-di-(*p*-hydroxyphenyl)-propane was employed as the fluorine-containing diol component for the synthesis of polyesters[22,29], polycarbonates[22,30], and polythiocarbonates[31]. Polyesters based on this diol and the dichlorides of isophthalic, terephthalic, and biphenyl-4,4′-dicarboxylic acids[22-29] and also polyesters based on trifluoromethyldi-(*p*-hydroxyphenyl)phenylmethane and the dichlorides of isophthalic and terephthalic acids[26,27] exhibit an enhanced stability with respect to thermal and thermo-oxidative degradation. Thus the temperatures of the onset of decomposition in nitrogen (data obtained by dynamic thermogravimetric analysis) of polyterephthalates obtained from the fluorine-containing diols hexafluoro-2,2-di-(*p*-hydroxyphenyl)-propane and trifluoromethyldi-(*p*-hydroxyphenyl)phenylmethane (438° and 446°C respectively) are higher than for the polyterephthalate obtained from 2,2-di-(*p*-hydroxyphenyl)propane (397°C).[27] On heating in air for 1 h at 400°C, these polymers lose 16.2, 11.5, and 26.3% of their weight respectively[32]. According to Ref. 29, sheet materials and aeroengine tubes made from polyesters and polycarbonates based on hexafluoro-2,2-di-(*p*-hydroxyphenyl)propane retain their characteristics after heating at 258°C for seven days.

Fluorine-containing polyesters based on the dichloride of 2,2-di-(*p*-carboxyphenyl)hexafluoropropane, which are distinguished by enhanced thermal stability, elasticity, and solubility, have also been described[27,28]. The synthesis of polyesters from *m*-derivatives of αω-diphenylperfluoroalkanes was reported in 1969.[33] Polyesters of the type



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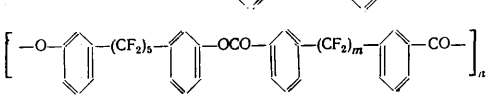
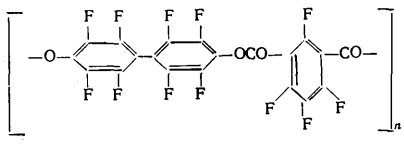


were obtained by the polycondensation of the dichlorides of -di-(*m*-carboxyphenyl)perfluoroalkanes with hexafluoropentanediol or αω-di-(*m*-hydroxyphenyl)perfluoropentane.

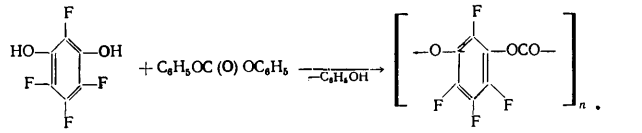
A polycarbonate based on αω-di-(*m*-hydroxyphenyl)-perfluoropentane has also been described[33]. The polymers synthesised in the same investigation have fairly low glass temperatures (16–45°C) and are elastomers above room temperature.

One of the attempts to modify the properties of polyesters consisted in their synthesis from aromatic perfluoro-compounds. A patent has been taken out[34] for high-molecular-weight polyesters which are resistant to thermal and thermo-oxidative degradation and which were synthesised by the interfacial polycondensation of octafluoro-4,4′-dihydroxybiphenyl with the dichlorides of tetrafluoroisophthalic and tetrafluoroterephthalic acids:



A similar polymer, consisting of a fluorinated analogue of Lavsan [a variety of nylon produced in the USSR (Ed. of Translation)] was obtained by the polycondensation of dimethyl tetrafluoroterephthalate and ethylene glycol; it differs little in its properties from Lavsan[35].

A patent[36] describes aromatic polyfluorocarbonates obtained by the polycondensation of tetrafluorophenylene bischloroformates with perfluorinated aromatic diols or 2,2-di-(*p*-hydroxyphenyl)propane. Poly(tetrafluoro-*m*-phenylene carbonate) was also synthesised by the polycondensation in the melt of tetrafluororesorcinol with diphenyl carbonate:



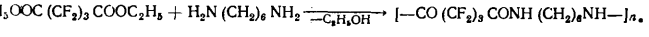
These polymers are suitable for the manufacture of articles designed for use at high temperatures.

III. FLUORINE-CONTAINING POLYAMIDE POLYMERS

1. Polyamides

The development of the chemistry of fluorine-containing polyamides was stimulated by the endeavour to synthesise a fluorinated analogue of nylon for the manufacture of fire-resistant fibres[37]. Like polyesters, fluorine-containing polyamides can be divided into three types. The polyamides and some of their properties are listed in Table 2.

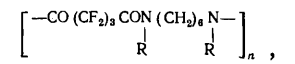
Aliphatic fluorine-containing polyamides were first described in patents at the beginning of the 1950's.[2,38] Polyamides of all three of the above types were obtained by the polycondensation of the diethyl esters or the dichlorides of alkane- and perfluoroalkane-dicarboxylic acids with hexamethylene- and 2,2,3,3,4,4,5,5-octafluorohexamethylene-1,6-diamine[38]. It proved possible to synthesise by this method only polyamides of the first type with a molecular weight (10000) sufficient for the preparation from them of fibre-forming materials:



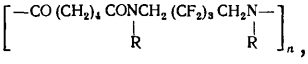
The fibres made from these polyamides have a high strength and density and are suitable for the manufacture of heavy fire-resistant fabrics. Analogous results were obtained in another study[39].

Later it was shown that, when solutions of diethyl perfluoroadipate are mixed with hexamethylenediamine, a low-molecular-weight polyamide is formed even in the cold, but its further polycondensation on heating in nitrogen or *in vacuo* is accompanied by degradation[40].

Fluorine-containing *N*-alkyl-substituted polyamides of the first type,



were synthesised by the polycondensation of secondary aliphatic diamines with dimethyl perfluoroglutarate, polyamides with the highest molecular weights being obtained from *NN′*-dimethyl and *NN′*-dimethyl-hexamethylenediamines. *N*-Substituted polyamides of the third type,



with a moderate molecular weight (degree of polymerisation 20–50%) could be obtained only from acid dichlorides, the reaction being carried out in a boiling inert solvent or in the presence of pyridine [41].

It was found that polyamides of the first type, like polyesters obtained from perfluoroalkanedicarboxylic acids, are hydrolysed very readily, the tendency towards hydrolysis decreasing somewhat with increasing dimensions of the substituent at the nitrogen atom [41].

It is noteworthy that chlorine-containing polyamides cannot be obtained by the polycondensation of hexamethylene- and octafluorohexamethylenediammonium salts of perfluoroadipic acid in the melt, since the salts decompose below the melting point. The attempts to achieve their polycondensation in the solid state at a temperature close to the melting point also failed to yield the expected results [39,40].

Although fluorine-containing diamines do not in fact form salts with weak acids owing to their low basicity, polyamides of the third type could nevertheless be obtained by heating the diamines with adipic acid [40,41].

In order to synthesise fluorine-containing polyamides of the first type, some investigators attempted to employ the methods of interfacial polycondensation using aliphatic [40,42,43] and aromatic [40] diamines and dichlorides of perfluoroalkanedicarboxylic acids. However, the polyamides obtained in this way proved to have low molecular weights. There is no doubt that the reason for the failure of these syntheses is the very ready hydrolysability of the dichlorides of perfluoroalkanedicarboxylic acids.

The high acylating capacity and volatility of such dichlorides made it possible to achieve the synthesis of fluorine-containing polyamides of the first type by a gas-phase polycondensation at the liquid–gas interface. High-molecular-weight fluorine-containing polyamides were obtained by passing the vapour of the dichloride of perfluoroadipic acid in a stream of nitrogen through aqueous solutions of aliphatic and aromatic diamines at 90–100°C. [40–46]

Attempts have been made to employ irreversible low-temperature polycondensation in amide solutions for the synthesis of fluorine-containing polyamides [47–49]. However, the aromatic polyperfluoroglutaramides obtained from the dichloride of perfluoroglutaric acid and benzidine or 3,3′-dihydroxybenzene in dimethylacetamide had very low molecular weights. Probably this is a consequence of the appreciably high rates of the competing reactions of dimethylacetamide with both the initial dichloride [50] and with the final acid chloride groups of the oligomers, resulting in chain termination.

A number of polyamides obtained from bifunctional derivatives of $\alpha\omega$-diphenylperfluoroalkanes have also been described. A thesis [51] mentions a high-melting polyamide made from hexamethylenediamine and 1,2-di-(*p*-carboxyphenyl)perfluoroethane. Mixed polyamides of this type with adipic or sebacic acid have been used to prepare thermostable fibres.

Recent patents [52,53] describe the synthesis of high-molecular-weight polyamides from *pp*′-dicarboxy- and *pp*′-diamino-derivatives of 2,2-diphenylhexafluoropropane. These polyamides are high-melting film-forming polymers with a comparatively high solubility.

Data on polyoxyamides and polyamides, obtained from derivatives of $\alpha\omega$-diphenylperfluoroalkanes and 2,2-diphenylperfluoropropane are presented in Table 2 and in Section IV, 2. A polyamide with aromatic perfluoro-units was obtained by heating octafluorobenzidine with pyromellitic dianhydride [54].

There has been only one study on the synthesis of fluorinated polyureas [55]. The polymers were obtained by the interfacial polycondensation of octafluorohexamethylenediamine with a number of di-isocyanates (hexamethylene, diphenylmethane, and toluylene di-isocyanates):

$$H_2NCH_2(CF_2)_4CH_2NH_2 + OCNRNCO \rightarrow [-NHCH_2(CF_2)_4CH_2NHCONHRNHCO-]_n .$$

The polymers synthesised had a low molecular weight and a relatively low thermal stability (decomposition temperature 215°C). [55]

2. Polyhydrazides

The possibility of obtaining low-molecular-weight fluorine-containing polyhydrazides from the dihydrazides and dichlorides of perfluoroalkane-dicarboxylic acids was first suggested by Brown in 1964 [61,62] (see Section IV, 2):

$$H_2NHNOC(CF_2)_mCONHNH_2 + ClOC(CF_2)_mCOCl \xrightarrow{-HCl} [-CONHNHCO(CF_2)_m-]_n .$$

High-molecular-weight aromatic poly(perfluoroalkylenebenzenedicarboxylic acid hydrazides) were synthesised by low-temperature polycondensation in amide solvents:

However, it was not possible to obtain high-molecular-weight fluorine-containing polyhydrazides by this method using the dichlorides of perfluoroalkanedicarboxylic acids. In order to avoid the chain termination of the macromolecules due to the considerable rate of reaction of the dichlorides of the strong perfluoroalkanedicarboxylic acids with the amide solvents, the dichlorides of aromatic acids were employed as the acid component and the dihydrazides of perfluoroalkanedicarboxylic acids as the diamine component (Table 3).

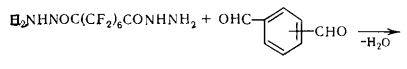
Aromatic poly(perfluoroalkylenebenzenedicarboxylic acid hydrazides) are amorphous polymers very readily soluble in the usual organic solvents; their softening temperatures are in the range 190–210°C and the temperatures of the onset of vigorous decomposition in air are between 250° and 300°C.

Polyisophthaloperfluoroglutarohydrazide, as well as polyisophthalohydrazide, form metal derivatives with zinc, nickel, and mercury salts.

Data on polyhydrazides based on 1,5-di-(*p*-carboxyphenyl)perfluoropentane [57] and 2,2-di-(*p*-carboxyphenyl)-perfluoropropane [63] are given in Table 3 and in Section IV, 2.

Fluorine-containing polyhydrazides are not of independent importance and are used as intermediates in the synthesis of certain polyazoles; the possibility of the cyclisation of fluorine-containing polyhydrazides into poly-1,3,4-oxadiazoles is discussed in Section IV, 2.

Fluorinated polymers obtained by the polycondensation of the dihydrazide of perfluorosuberic acid with isophthalaldehyde and terephthalaldehyde ($\eta_{inh} \simeq 0.1$) have also been described [64]:



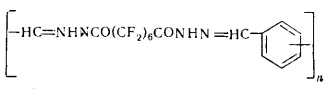


Table 2. Fluorine-containing polyamides.

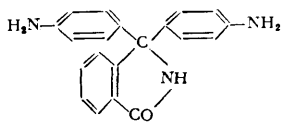
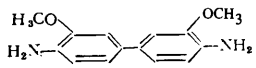
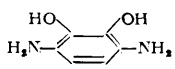
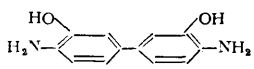
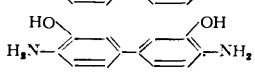
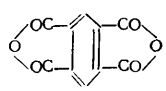
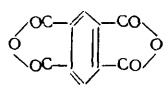
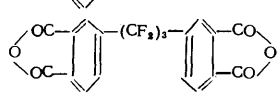
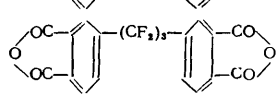
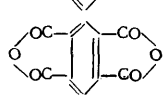
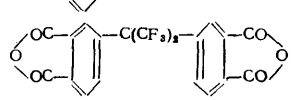
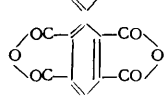
Initial component: amines	Initial component: acids and their derivatives	Certain properties of polymers	References
$(CH_2)_2(NH_2)_2$	$(CF_2)_4(COCl)_2$	$\eta_{inh} = 0.12$, $T_f = 280°C$	44—46
$(CH_2)_6(NH_2)_2$	$(CF_2)_3(COOC_2H_5)_2$	$T_f = 183-185°C$	38
$(CH_2)_6(NH_2)_2$	$(CF_2)_4(COCl)_2$	$\eta_{inh} = 0.2-0.5$, $T_f = 210°C$	40, 42—46
$(CH_2)_6(NH_2)_2$	$(CF_2)_4(COOC_2H_5)_2$	$\eta_{inh} = 0.08$, $T_f \simeq 200°C$; sol. in DMFA	38—40
$(CH_2)_6(NH_2)_2$	$(CF_2)_5(COCl)_2$		44—46
$(CH_2)_6(NH_2)_2$	$(CF_2)_2CH_4COX)_2$*	$T_f = 400°C$	51
$(CH_2)_6(NH_2)_2$	$C(CF_3)_2(C_6H_4COCl)_2$	$\eta_{inh} = 0.24$, $T_f = 280°C$; sol. in DMFA	53
$(CH_2)_6(NH_2)_2$	$(CF_2)_4(COCl)_2$	$\eta_{inh} = 0.21$, $T_f = 175-180°C$	40
$(CH_2)_n(NH_2)_2$	$(CF_2)_4(COOC_2H_5)_2$		42
$(CH_2)_6(NHCH_3)_2$	$(CF_2)_3(COOCH_3)_2$	$T_{brittle} = 25-30°C$; sol. in DMFA and acetone	41
$(CH_2)_6(NHC_2H_5)_2$	$(CF_2)_3(COOCH_3)_2$	$T_{brittle} = 5°C$; sol. in DMFA and acetone	41
$(CH_2)_6(NHC_3H_7\text{-}i)_2$	$(CF_2)_3(COOCH_3)_2$	$T_{brittle} = 20°C$; sol. in DMFA and acetone	41
$(CH_2)_6(NHC_4H_9\text{-}n)_2$	$(CF_2)_3(COOCH_3)_2$	$T_{brittle} = 20°C$; sol. in DMFA, benzene, iso-octane, and chloroform	41
$p\text{-}C_6H_4(NH_2)_2$	$(CF_2)_4(COCl)_2$	$\eta_{inh} = 0.09$, $T_f = 378°C$ (decomp.)	40
$p\text{-}C_6H_4(NH_2)_2$	$(CF_2)_4(COCl)_2$	$\eta_{inh} = 0.64$, $T_f > 380°C$	44—46
$m\text{-}C_6H_4(NH_2)_2$	$(CF_2)_4(COCl)_2$	$\eta_{inh} = 0.46$	44—46
$p\text{-}C_6H_4(CH_2NH_2)_2$	$(CF_2)_4(COCl)_2$	$\eta_{inh} = 0.10$, $T_f = 258-264°C$	40
$(C_6H_4NH_2\text{-}p)_2$	$(CF_2)_3(COCl)_2$	$\eta_{log} = 0.16$, $T_{decomp} = 250°C$	47—49
$m\text{-}C_6H_4(NH_2)_2$	$C(CF_3)_2(C_6H_4COCl\text{-}p)_2$	$\eta_{inh} = 0.43$, $T_f = 370°C$ (decomp.); sol. in DMFA and DMAA	53
$1,2,6\text{-}C_6H_3(CH_3)(NH_2)_2$	$C(CF_3)_2(C_6H_4COCl\text{-}p)_2$	$\eta_{inh} = 0.81$, $T_f > 350°C$	52
$(C_6H_4NH_2\text{-}p)_2$	$C(CF_3)_2(C_6H_4COCl\text{-}p)_2$	$\eta_{inh} = 1.08$, $T_f > T_{decomp} \simeq 410°C$; sol. in DMFA and DMAA	53
$SO_2(C_6H_4NH_2\text{-}p)_2$	$C(CF_3)_2(C_6H_4COCl\text{-}p)_2$	$\eta_{inh} = 0.7$, $T_f > 350°C$	52
$C(CH_3)_2(C_6H_4NH_2\text{-}p)_2$	$C(CF_3)_2(C_6H_4COCl\text{-}p)_2$	$\eta_{inh} = 1.14$, $T_f > 400°C$	52
	$C(CF_3)_2(C_6H_4COCl\text{-}p)_2$	$\eta_{inh} = 0.44$, $T_f > T_{decomp.} = 390°C$; sol. in DMFA and DMAA	53
	$C(CF_3)_2(C_6H_4COCl\text{-}p)_2$	$\eta_{inh} = 1.1$, $T_f > 375°C$	52
$CF_2)_4(CH_2NH_2)_2$	$(CF_2)_4(COCl)_2$	$\eta_{inh} = 0.11$, $T_f = 253°C$	40
$(CF_2)_4(CH_2NH_2)_2$	$(CF_2)_4(COOC_2H_5)_2$	$\eta_{inh} = 0.03$, $T_f = 231°-232°C$; sol. in DMFA	38, 40
$C(CF_3)_2(C_6H_4NH_2\text{-}p)_2$	$C(CF_3)_2(C_6H_4COCl_2)$	$\eta_{inh} = 0.7$, $T_f = 400°C$; sol. in DMFA and acetone	52, 53
$(CF_2)_4(CH_2NH_2)_2$	$(CH_2)_4(COCl)_2$	$\eta_{inh} = 0.21$, $T_f = 216-223°C$	40
$(CF_2)_4(CH_2NH_2)_2$	$(CH_2)_4(COOC_2H_5)_2$	$\eta_{inh} = 0.30$, $T_f = 219-221°C$; sol. in hot DMFA	38, 40
$(CF_2)_3(CH_2NHCH_3)_2$	$(CH_2)_4(COCl)_2$	$T_{brittle} = 25-30°C$; sol in acetone and DMFA	41
$(CF_2)_3(CH_2NHC_2H_5)_2$	$(CH_2)_4(COCl)_2$	$T_{brittle} = 20°C$; sol. in acetone, chloroform and DMFA	41

Table 2 cont'd

Initial component: amines	Initial component: acids and their derivatives	Certain properties of polymers	References
$(CF_2)_3(CH_2NHC_3H_7\text{-}iso)_2$	$(CH_2)_4(COCl)_2$	$T_{brittle}$ = 30-35°C; sol. in acetone, chloroform, benzene, toluene, and DMFA	41
$(CF_2)_3(CH_2NHC_4H_9\text{-}n)_2$	$(CH_2)_4(COCl)_2$	$T_{brittle}$ = 10-15°C; sol. in acetone, chloroform, benzene, toluene, ethyl acetate, and DMFA	41
$C(CF_3)_2(C_6H_4NH_2\text{-}p)_2$	$p\text{-}C_6H_4(COCl)_2$	η_{inh} = 0.6, T_f > 400°C	52
$C(CF_3)_2(C_6H_4NH_2\text{-}p)_2$	$p\text{-}C_6H_4(COCl)_2$	η_{inh} = 1.48, $T_f \approx$ 370°C (decomp.); sol. in DMFA and DMAA	53
$C(CF_3)_2(C_6H_4NH_2\text{-}p)_2$	$m\text{-}C_6H_4(COCl)_2$	η_{inh} = 0.65, T_f = 348°C	52
$C(CF_3)_2(C_6H_4NH_2\text{-}p)_2$	$1,3,5\text{-}C_6H_3(COCl)_2C_4H_9$	η_{inh} = 0.72, T_f > 350°C	52
$C(CF_3)_2(C_6H_4NH_2\text{-}p)_2$	$1,3,5\text{-}C_6H_3(COCl)_2Cl$	η_{inh} = 0.74, T_f > 350°C	52
	$(CF_2)_3(COCl)_2$	η_{log} = 0.16	47, 48
	$(CF_2)_5(C_6H_4COCl)_2$	η_{log} = 0.8; sol. in amide solvents; d_{25}^4 = 1.54	56, 57
	$(CF_2)_6(C_6H_4COCl)_2$	η_{log} = 0.6; sol. in amide solvents, d_{25}^4 = 1.59	56, 57
$(CF_2)_6(C_6H_4NH_2\text{-}m)_2$		η_{log} = 1.5; sol. in amide solvents	56, 57
$(CF_2)_6(C_6H_4NH_2\text{-}m)_2$		η_{log} = 1.5; sol. in amide solvents	56, 57
$O(C_6H_4NH_2\text{-}p)_2$		η_{inh} = 1.65	33, 58, 59
$O(C_6H_4NH_2\text{-}m)_2$		η_{inh} = 0.51	33, 58
$C(CF_3)_2(C_6H_4NH_2\text{-}p)_2$		η_{inh} = 0.6	60
$C(CF_3)_2(C_6H_4NH_2\text{-}p)_2$		η_{inh} =0.52	60
$(C_6F_4NH_2\text{-}p)_2$			54

*In the original paper it is not stated whether the acid or its derivative was employed.

3. Polyurethanes

Fluorine-containing polyurethanes were first obtained in 1954 by heating hexafluoropentanediol with hexamethylene, toluylene, and octafluorotetramethylene di-isocyanates at 150°C.[65] These polyurethanes have been suggested as thermostable coatings. The fluorine-containing polyurethanes described in the literature and some of their properties are presented in Table 4.

Many polyurethanes containing fluorine in both the diol and in the di-isocyanate components of the molecule, including aromatic perfluoropolyurethanes have been described[66,67]. They were synthesised from fluorine-containing compounds in two ways: (1) by the reaction of di-isocyanates with diols (in solution and in the melt) and (2) by the reaction of diamines with bischloroformates (in solution under the conditions of interfacial polycondensation). For example, the synthesis of poly-[(*N*-hexafluorotrimethylene)hexafluoropentamethylene

Table 3. Fluorine-containing polyhydrazides.

Polymer unit	Certain properties	References
$-(CF_2)_3CONHNHCO-$		61, 62
$-NHNHCO(CF_2)_3CONHNHCO-C_6H_4-CO-$	η_{log} = 0.26; sol. in alcohol, DMSO, and amide solvents; amorph.	48
$-NHNHCO(CF_2)_3CONHNHCO-C_6H_4-CO-$	η_{log} = 0.84; sol. in alcohol, acetone, DMSO, and amide solvents	47, 48
$-NHNHCO(CF_2)_3CONHNHCO-C_6H_4-CO-$	η_{log} = 0.86; sol. in methanol, DMSO, and amide solvents; amorph.	47, 48
$-NHNHCO-(CF_2)_4CONHNHCO-C_6H_4-CO-$	η_{log} = 0.89; sol. in alcohol acetone, DMSO, and amide solvents; amorph.	48
$-NHNHCO-C_6H_4-(CF_2)_3-C_6H_4-CONHNHCO-O-C_6H_4-CO-$	η_{log} = 0.35; sol. in DMSO and amide solvents	57
$-C_6H_4-C(CF_3)_2-C_6H_4-CONHNHCO-$	η_{inh} = 0.81; sol. in DMFA; T_{soft} = 340°C	63
$-NHNHCO-C_6H_4-C(CF_3)_2-C_6H_4-CONHNHCO-C_6H_4-CO-$	η_{inh} = 0.79; sol. in DMFA; T_{soft} = 360°C	63
$-NHNHCO-C_6H_4-C(CF_3)_2-C_6H_4-CONHNHCO-C_6H_4-CO-$	η_{inh} = 0.67; sol. in DMFA; T_{soft} = 330°C	63

dicarbamate] was achieved by heating hexafluorotrimethylene di-isocyanate with hexafluoropentanediol in ethyl acetate in the presence of triethylamine:

$$OCN(CF_2)_3NCO + HOCH_2(CF_2)_3CH_2OH \rightarrow [-NH(CF_2)_3NHC(O)OCH_2(CF_2)_3CH_2OCO-]_n \xrightarrow{H_2O} HOOCCF_2COOH + H_2NCOOCH_2(CF_2)_3CH_2OCONH_2 .$$

This polyurethane is readily hydrolysed in air to hexafluoropentylene dicarbamate. On heating in the absence of moisture at 80–90°C, the polyurethane splits off hydrogen fluoride and is apparently converted into the polymer $[-N{=}CFCF_2CF{=}NCOOCH_2(CF_2)_3CH_2OCO-]_n$, which is somewhat more resistant to hydrolysis.

Polyurethanes in which a methylene group separates the perfluoroalkylene chain from the nitrogen atom, which some investigators believe makes them more resistant to hydrolysis, were synthesised by the reaction of fluorine-containing bischloroformates with diamines. Thus, on heating hexafluoropentamethylene bischloroformate with hexafluoropentamethylenediamine in ethyl acetate in the presence of pyridine, poly-[(*N*-hexafluoropentamethylene)-hexafluoropentamethylene dicarbamate] is formed:

$$ClOCOCH_2(CF_2)_3CH_2OCOCl + H_2NCH_2(CF_2)_3CH_2NH_2 \xrightarrow{-HCl} \rightarrow [-NHCH_2(CF_2)_3CH_2NHCOOCH_2(CF_2)_3CH_2OCO-]_n .$$

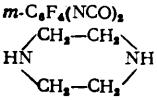
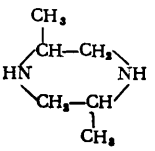
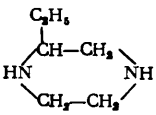
Under the conditions of interfacial polycondensation, the same reaction is accompanied by extensive hydrolysis of the bischloroformate. Unfortunately the authors do not quote experimental data for the hydrolytic stability for the polymer itself.

An aromatic perfluoropolyurethane was obtained by the reaction of tetrafluoro-*m*-phenylene di-isocyanate with tetrafluorohydroquinone in boiling xylene [66,67]. Among the fluorine-containing polyurethanes synthesised by Hollander and coworkers [66,67], the most thermostable is poly-[(*N*-tetrafluoro-*p*-phenylene)hexafluoropentamethylene dicarbamate], the decomposition temperature of which is about 300°C; other fluorine-containing polyurethanes decompose at about 200°C. [67]

The effect of fluorine atoms in the diol or di-isocyanate unit of the polymer on the properties of aliphatic polyurethanes was also investigated in other studies [68,69]. It was found, for example, that the polyurethane $[-NHCH_2(CF_2)_4CH_2NHCOO(CH_2)_6OCO-]_n$, containing in the di-isocyanate component a perfluoromethylene chain separated from the nitrogen atom by a methylene group, surpasses in its thermal stability the polyurethane $[-HN(CH_2)_6NHCOOCH_2(CF_2)_4CH_2OCO-]_n$ and a non-fluorinated analogue (weight losses *in vacuo* at 215°C over a period of 3.5 h about 1.5, 20, and 50% respectively). The first polyurethane is somewhat more resistant to the action of acids than the non-fluorinated polyurethane, but is inferior to it as regards resistance to the action of alkalis.

Polyurethanes based on fluorine-containing polyesters and polyethers with terminal hydroxy-groups [for example poly(hexafluoropentamethylene adipate), poly-hexafluoropentamethyleneformyl, etc.] and aromatic di-isocyanates or perfluorodi-isocyanates have also been

Table 4. Fluorine-containing polyurethanes.

Initial components		Certain properties of polymers	References
isocyanates and amines	glycols and bischloroformates		
$(CH_2)(NCO)_2$	$(CF_2)_3(CH_2OH)_2$		65
$(CH)_3(NCO)_3$	$(CF_2)_4(CH_2OH)_2$	$[\eta] = 0.3$, $T_f = 126°C$; cryst.	69
$1,3,5\text{-}C_6H_4(CH_3)(NCO)_2$	$(CF_2)_3(CH_2OH)_2$		65
$p\text{-}C_6H_4(NCO)_2$	$(CF_2)_3(CH_2OH)_2$	Solid; $T_f = 190-196°C$	66, 67
$(CF_2)_3(NCO)_2$	$(CF_2)_3(CH_2OH)_2$	Rubberlike substance	66, 67
$(CF_2)_4(NCO)_2$	$(CF_2)_3(CH_2OH)_2$		65
$(CF_2)_3(CH_2NH_2)_2$	$(CF_2)_3(CH_2OCOCl)_2$	$T_{decomp} \simeq 200°C$ (air, helium)	66, 67
$(CF_2)_3(CH_2NH_2)_2$	$p\text{-}C_6F_4(OCOCl)_2$	$T_{soft} = 175-179°C$, $T_{decomp} \simeq 200°C$	66, 67
$p\text{-}C_6F_4(NCO)_2$	$(CF_2)_3(CH_2OH)_2$	Waxy substance; $T_f > 340°C$, $T_{decomp} \simeq 300°C$ (air, helium)	66
$m\text{-}C_6F_4(NCO)_2$	$(CF_2)_3(CH_2OH)_2$	Colourless solid; films formed from melt	66, 67
$m\text{-}C_6H_4(NCO)_2$	$p\text{-}C_6F_4(OH)_2$	Solid infusible substance; $T_{decomp} \simeq 200°C$ (air, helium)	66, 67
$(CF_2)_4(CH_2NH_2)_2$	$(CH_2)_6(OCOCl)_2$	$[\eta] = 0.7$, $T_f = 184°C$; cryst.	68, 69
$p\text{-}C_6F_4(NCO)_2$	$(CH_2)_6(OCOCl)_2$	$T_f = 280-281°C$; cryst.	66, 67
$m\text{-}C_6F_4(NCO)_2$	$(CH_2)_6(OCOCl)_2$		66
	$C(CF_3)_2(C_6H_4OCOCl\text{-}p)_2$	$\eta_{inh} = 0.57$, $T_f = 260°C$	75
	$C(CF_3)_2(C_6H_4OCOCl\text{-}p)_2$	$\eta_{inh} = 1.60$, $T_f = 300°C$	75
	$C(CF_3)_2(C_6H_4OCOCl\text{-}p)_2$	$\eta_{inh} = 0.82$, $T_f = 285°C$	75
$m\text{-}C_6H_4(NH_2)_2$	$C(CF_3)_2(C_6H_4OCOCl\text{-}p)_2$	$\eta_{inh} = 0.30$, $T_f = 238°C$	75
$p\text{-}C_6H_4(CH_2NH_2)_2$	$C(CF_3)_2(C_6H_4OCOCl\text{-}p)_2$	$\eta_{inh} = 0.40$	75
$CH_2(cis\text{-}C_6H_{10}NH_2\text{-}4)_2$	$C(CF_3)_2(C_6H_4OCOCl\text{-}p)_2$	$\eta_{inh} = 1.16$, $T_f = 210°C$	75
$p\text{-}C_6H_4[C(CH_3)_2NH_2]_2$	$C(CF_3)_2(C_6H_4OCOCl\text{-}p)_2$	$\eta_{inh} = 0.33$, $T_f = 200°C$	75

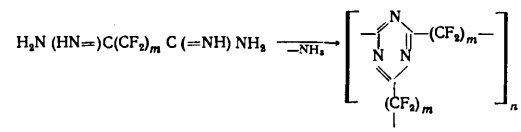
described. Polyurethanes obtained from polyperfluoroethers may find application as elastomers, coatings, adhesives, etc., i.e. whenever elasticity at low temperatures and high chemical stability are required [10,70,74].

A patent was published in 1968 describing the synthesis of high-molecular-weight polyurethanes based on the bischloroformate of 2,2-di-(4-hydroxyphenyl)hexafluoropropane and various diamines. It is suggested for the manufacture of light-resistant flexible sheets and crease-resistant fibres [75].

IV. FLUORINE-CONTAINING POLYAZOLES

1. Poly-1,3,5-triazines

The first examples of the class of polyperfluoroalkylene-heterocycles, namely polyperfluoroalkylene-1,3,5-triazines, were obtained towards the end of the 1950's and at the beginning of the 1960's by the homocondensation of the diamidines or imidines of perfluoroalkanecarboxylic acids and their copolycondensation with the monoamidines of perfluoroalkanecarboxylic acids [76-80]. Thus, on heating perfluoroadipodiamidine or perfluoroglutarimidine above the melting point, solid insoluble and infusible cross-linked polymers are formed:

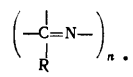


The use of mixtures of a diamidine (or imidine) with a monoamidine for polycondensation leads to the formation of partly cross-linked polymers, the degree of cross-linking and the properties of which depend on the molar ratios of the components and the length of their perfluoromethylene chain. The copolymers are either elastomeric materials with a low strength or they are rigid non-elastic

polymeric substances. All polyperfluorotriazines have a very high chemical stability and a high resistance to thermal and thermo-oxidative degradation. For example, the copolymers of perfluoroadipodiamidine or perfluoroglutarimidine with perfluorobutyramidine (1 : 1) are stable on heating in air at 350°C for about 72 h. Boiling in fuming nitric acid for 24 h leads only to a change of their colour from yellow to white.

The thermal degradation of polyperfluoroalkylenetriazines was investigated by a number of workers. It has been shown [81,82] that the activation energy for the degradation reactions of these polymers (homo- and co-polymers) is about 30–40 kcal mole^{-1} below 500°C, which is much less than the activation energy for the thermal decomposition of Teflon (about 80 kcal mole^{-1}); at about 500°C the rates of their decomposition are lower than that of Teflon.

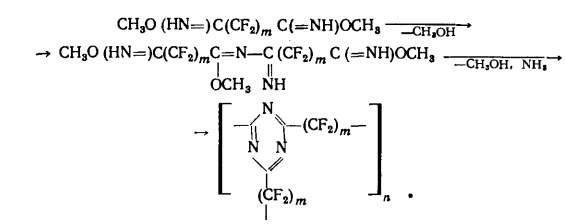
Other investigations [83] showed that the rate of degradation of polyperfluoroalkylenetriazines at 350–500°C *in vacuo* falls rapidly with increasing conversion up to 30% and then remains almost constant up to complete volatilisation of the polymer. While the rate of degradation in the initial stage is comparable with the rate of degradation of Teflon, in the second stage it is much lower. The authors suggest that the high rates of degradation in the initial stages are due to the amide groups, which are always present in the polymers. The decomposition of their amide groups results in the formation of water, which hydrolyses the triazine rings, and radicals, which cause their polymerisation with formation of a polyene structure:



After the amide groups have been consumed, the main degradative pathway reduces to the depolymerisation of the comparatively short perfluoroalkylene fragments of the macromolecule with chain transfer by the transalkylation of the triazine rings. The rates of these reactions are lower than the rate of depolymerisation of Teflon.

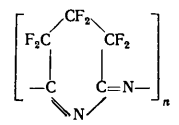
Since polyperfluoroalkylenetriazines were of greater interest as very promising elastomers [84], the efforts of many investigators were directed to the development of other methods for their synthesis, including methods for the synthesis of polytriazines with a linear structure.

Cross-linked polyperfluoroalkylenetriazines similar to those described above were obtained by the thermal homopolycondensation of dimethyl perfluoroglutarimidate and dimethyl perfluoroadipimidate and their "dimers": [85–87]



Later a similar conversion of dimethyl perfluoroglutarimidate into a cross-linked triazine polymer was also described in another study [88].

The trimerisation reaction of the dinitriles of perfluoroalkanedicarboxylic acids, the possibility of which in the presence of acid or alkaline catalysts and had been pointed out previously [79], was investigated. The homopolycyclisation of perfluoroglutarodinitrile under a high pressure (about 20 000 kgf cm^{-2}) in the presence of ammonia or secondary amines at 276°C leads to polytriazines. When the pressure is reduced, the formation of polymers with the structure [89]



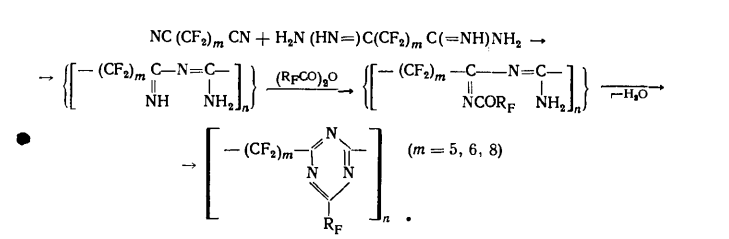
predominates.

A method for the preparation of cross-linked polytriazines by the polycyclisation of fluorine-containing dinitriles in the presence of metals (copper, iron, etc.) at 190°C has been described [90]. Polycondensation of perfluoroglutarodinitrile in the presence of metal oxides (Ag_2O, HgO, etc.) leads to a low-molecular-weight polymer (ηinh = 0.03) containing the group $-C=N-C=N-$. [91,92]

A method for the preparation of polytriazine by the thermal homopolycondensation or copolycondensation of perfluorodinitriles containing ether linkages [for example, 2,7-dicyano-3-oxaperfluoroheptane $NCCF(CF_3)O(CF_2)_4CN$ and 2,10-dicyano-3,9-dioxaperfluoroundecane $NCCF(CF_3)O(CF_2)_5OCF(CF_3)CN$] in the presence of ammonia has been patented. The cotrimerisation of the above dinitriles with diamidines derived from them or of diamidines with mononitriles (for example, with perfluoroacetonitrile and perfluoro-2-propoxypropionitrile) in an amount of 0.5–30% has also been described. In contrast to the polymers obtained from derivatives of perfluoroalkanedicarboxylic acids, these resins have satisfactory mechanical characteristics, which allows their use for the manufacture of mechanically strong articles [93,94].

A patent [95] proposes a method for the synthesis of perfluoroalkylenetriazines by heating at 50°C a mixture of perfluoroglutarothioamide with perfluorobutyronitrile in the presence of triethylamine.

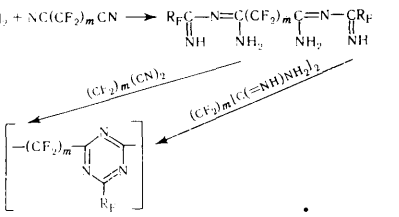
The first reports of the synthesis of linear polyperfluoroalkylenetriazines were published almost simultaneously by a number of investigators. According to the method proposed by Dorfman et al. [96] and by Griffin [97], the reaction of diamidines of perfluoroalkanedicarboxylic acids with dinitriles of perfluoroalkanedicarboxylic acids was used to synthesise initially at room temperature linear imidoylamidine polymers which, without isolation, were acylated and cyclodehydrated by anhydrides of perfluorocarboxylic acids to polyperfluoroalkylenetriazines:



This method was employed to synthesise from derivatives of perfluoroalkanedicarboxylic acids linear-high-molecular-weight polytriazines (degree of polymerisation about 300), which are soluble yellow rubberlike polymers with a glass temperature between −5 and −17°C and a decomposition temperature of about 420°C (differential thermal analysis).

The attempt [96] to obtain an imidoylamidine polymer by the reaction of dinitriles with ammonia without isolating the diamidines yielded only low-molecular-weight products.

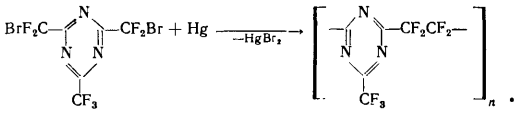
In another method [97,98] a stable intermediate bisimidoylamidine compound is initially obtained from a monoamidine and a dinitrile and isolated in the solid state; after purification it is refluxed in benzene with a diamidine or a dinitrile until the formation of a linear elastomer:



If the above processes are carried out without the isolation and purification of the intermediate, a gel is formed.

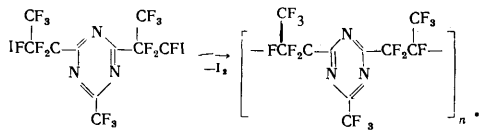
Methods have also been proposed for the preparation of polyperfluoroalkylenetriazines from monomers already containing triazine rings.

An interesting method has been described [91,97,99,100] for the preparation of a high-molecular-weight polytriazine from 2,4-di(bromodifluoromethyl)-6-trifluoromethyltriazine by heating it with mercury in evacuated tubes at 200°C (degree of polymerisation about 350):



An analogous polymer was obtained [100] by the same method from 2,4-di(difluoroiodomethyl)-6-difluoromethyltriazine. According to Griffin [97], the polymer exhibits elastic properties above 40°C. The author suggests that the glass temperature of this polymer may be reduced by introducing into the triazine rings of the macromolecules longer perfluoroalkyl substituents.

A polytriazine elastomer has been obtained by the radical polycondensation of di(iodoperfluoroalkyl)triazine under the influence of ultraviolet light:



The scope of this method is limited by the low availability of the initial di-iodide.

The thermal and chemical stabilities of linear high-molecular-weight polytriazines are comparable to the stability of cross-linked polymers but, as was expected, their mechanical strength proved to be much higher (the tensyl strength of linear polytriazine is 98 kgf cm^{-2} [97] against 7–35 kgf cm^{-2} [96] for cross-linked polymers).

The possibility of obtaining polytriazines from monomers containing triazine rings and cyanoperfluoroalkyl groups is considered in a brief report [90].

2. Other Polyazoles

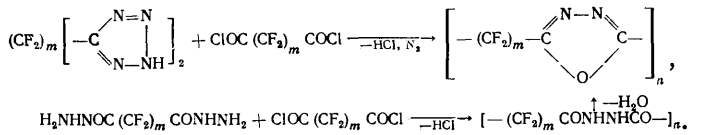
Simultaneously with the development of methods for the synthesis of linear polyperfluoroalkylene-1,2,3-triazines, the possibility of synthesising other high-molecular-weight linear polyperfluoroalkyleneazoles was investigated.

Numerous model perfluoroalkyl-substituted heterocyclic systems were obtained even earlier and it was established that their chemical and thermal stabilities are comparable to those of fluorinated triazine systems [80,101].

Towards the first half of the 1960's, methods of synthesising various high-molecular-weight linear polyazoles containing aliphatic and aromatic units in the macromolecular chain were already known. It was possible to postulate that the use of these methods for the synthesis of fluorine-containing polyazoles will make the latter more readily available than linear polytriazines.

Indeed, soon after the first publications on cross-linked polyfluoroalkylenetriazines, several communications appeared on the synthesis of other fluorine-containing polyazoles: poly-1,3,4-oxadiazoles, polybenzoxazoles, polybenzimidazoles, etc. These polyazoles were linear polymers with relatively low molecular weights.

The synthesis of polyperfluoroalkylene-1,3,4-oxadiazoles was achieved by two methods [61,62,102]; in the first method polyoxadiazoles were obtained by treating solutions of bistetrazoles in pyridine or acetonitrile with dichlorides of perfluoroalkanedicarboxylic acids:

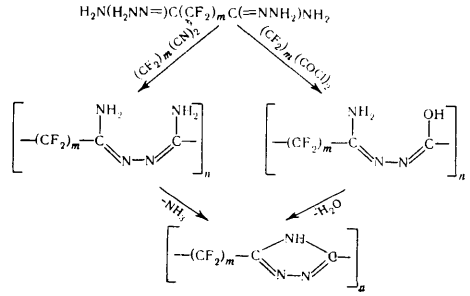


A polyoxadiazole (η_{inh} = 0.1), which behaves as an elastomer in the range 65–120°C and is inert at 100°C to the action of concentrated sulphuric and nitric acids, was synthesised in this way from perfluorohexane-1,6-bistetrazole and the dichloride of perfluorosuberic acid [61,62,102].

In the second method, polyhydrazides, which were subsequently converted into polyperfluoroalkyleneoxadiazoles, were obtained from the dihydrazides and dichlorides of perfluoroalkanedicarboxylic acids. The conditions for the preparation of the polyhydrazides and their cyclisation and also the characteristics of the polymers were not quoted [61,62] apart from the mention of a comparatively low molecular weight.

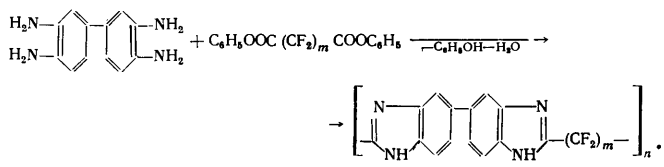
It is noteworthy that aromatic polyperfluoroalkylenehydrazides (see Section III, 2) do not undergo thermal cyclisation to polyoxadiazoles. Chemical cyclodehydration of these polyhydrazides with phosphorus oxychloride is accompanied by marked degradation and leads to low-molecular-weight compounds [48].

Two pathways for the preparation of polyperfluoroalkylene-1,2,4,4*H*-triazoles from perfluoroalkylenediacyldihydrazidines have been indicated [62]:



In the first method perfluoroalkylenediacyldihydrazidine reacts with a perfluoroalkylenedinitrile giving a polymer, which is converted into poly-1,2,4,4*H*-triazole with liberation of ammonia. In the second method perfluoroalkylenediacyldihydrazidine is acylated by the dichloride

of a perfluoroalkanedicarboxylic acid and the resulting polymer is dehydrated to poly-1,2,4,4*H*-triazole. These methods of synthesis of triazoles are similar to the modern methods for the synthesis of linear polyperfluoroalkylenetriazines from the diamidines of perfluoroalkanedicarboxylic acids (see Section IV, 1). In 1964 a number of investigators described almost simultaneously the synthesis of low-molecular-weight polyperfluoroalkylenebenzimidazoles by the polycondensation in the melt of 3,3-diaminobenzidine with the diphenyl esters of various perfluoroalkanedicarboxylic acids [103-105]:

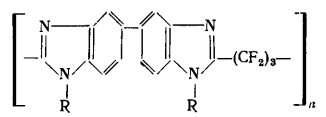


Contrary to expectation, these polymers proved to be inadequately thermostable and their degradation with liberation of hydrogen fluoride was observed in the polycondensation process itself in an atmosphere of argon below 250°C. [104,105] According to thermogravimetric data, the temperature of the onset of vigorous decomposition of polyperfluoroalkylbenzimidazoles in nitrogen does not exceed 300°C. [103] It has been noted [104] that polycondensation with perfluoroglutaric acid (at 220–250°C) leads to marked charring of the reaction mixture.

In the polycondensation of 3,3′-diaminobenzidine with both perfluoroglutaric acid and with its diphenyl ester, the evolution of not only hydrogen fluoride but also carbon dioxide was observed [106].

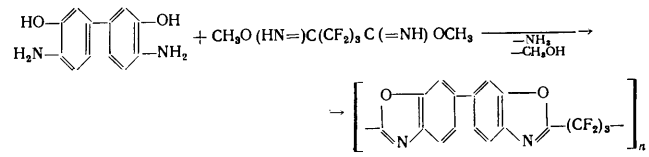
The comparatively low thermal stability of poly-2,2′-(perfluoroalkylene)-5,5′-dibenzimidazoles can be explained by a dehydrofluorination reaction, which is attributed mainly to the mobility of the hydrogen atoms in the imino-groups of the benzimidazole rings [104,107]. This hypothesis was confirmed to some extent by the appreciable increase of the decomposition temperatures of model *N*-methyl- and *N*-phenyl-substituted 2-perfluoroalkylbenzimidazoles ($T_{decomp} \simeq 390$–450°C) compared with unsubstituted 2-perfluoroalkylbenzimidazoles ($T_{decomp} \simeq 300$°C). [49,107]

N-Substituted fluorine-containing polybenzimidazoles were obtained by the polycondensation in the melt of 4,4′-di(methylamino)-3,3′-diaminobiphenyl and 4,4′-dianilino-3,3′-diaminobiphenyl with diphenyl perfluoroglutarate [49]:



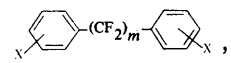
The study of their thermal stability *in vacuo* and in air showed that only phenylation at nitrogen leads to some improvement of thermal stability: poly-(*NN*′-diphenyl-2,2′-perfluorotrimethylene-5,5′-dibenzimidazole) begins to decompose very slowly at about 350°C in air and *in vacuo*. The appreciable difference between the behaviour of model fluorine-containing benzimidazoles and the corresponding polymers can be explained by the presence in the latter of a relatively large number of terminal amino-groups as a result of their low molecular weight.

It was found useful to attempt the replacement of the imino-group in the ring by an oxygen atom, i.e. to obtain a benzoxazole structure. A low-molecular-weight poly-2,2′-perfluorotrimethylene-6,6′-dibenzoxazole was obtained by the polycondensation of 3,3′-dihydroxybenzidine with dimethyl bisiminoperfluoroglutarate in *N*-methylpyrrolidone at 190°C; its properties were not investigated [108]:



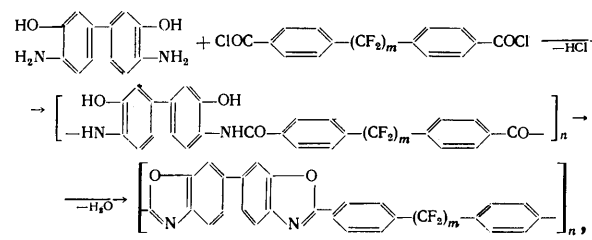
It follows from the above that fairly numerous attempts to achieve the synthesis of polyazoles with perfluoromethylene bridges in the chain from derivatives of perfluoroalkanedicarboxylic acids led only to low-molecular-weight polymers (with the exception of polytriazines).

High-molecular-weight linear polyperfluoroalkyleneazoles were obtained successfully for the first time from derivatives of $\alpha\omega$-diphenylperfluoroalkanes—monomers with functional groups of the type



where X = *p*-COCl, *m*-NH_2, etc., "screened" from the perfluoromethylene chain. In these compounds thermostable benzene rings serve as a "screen" [33,56-59,109].

Thus high-molecular-weight polybenzoxazoles were obtained by a two-stage synthesis from the dichlorides of $\alpha\omega$-di-(*p*-carboxyphenyl)perfluoroalkanes and 3,3′-dihydroxybenzidine via poly-*o*-hydroxyamides with their subsequent thermal cyclisation (250–300°C) in a vacuum or by chemical treatment (polyphosphoric acid, 200°C). [56,57,109] The polybenzoxazoles synthesised by the first method,



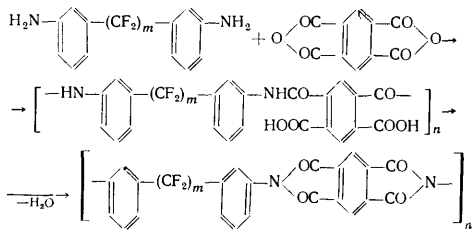
are insoluble, probably owing to partial cross-linking. On cyclisation under milder conditions in polyphosphoric acid, soluble polymers are formed ($\eta\log = 0.5$–1.3). However, under these conditions there is partial hydrolysis of CF_2 groups adjacent to the benzene rings.

High-molecular-weight soluble polybenzimidazoles ($\eta\log = 1.1$–1.6) were synthesised by the polycondensation in the melt of 3,3′-diaminobenzidine with diphenyl esters of $\alpha\omega$-di-(*p*-carboxyphenyl)perfluoroalkanes [56,57,109].

Polyperfluoroalkylene-1,3,4-oxadiazole was obtained by the condensation of the dihydrazide of 1,5-di-(*p*-carboxyphenyl)perfluoropentane with isophthaloyl chloride in hexamethylphosphoramide followed by cyclisation of the resulting polyhydrazide [57,109]. In contrast to the polyhydrazides obtained from derivatives of perfluoroalkanedicarboxylic acids [48], heat treatment of this polyhydrazide resulted in its conversion into a poly-1,3,4-oxadiazole.

High-molecular-weight polyperfluoroalkyleneimides have been synthesised by various investigators from

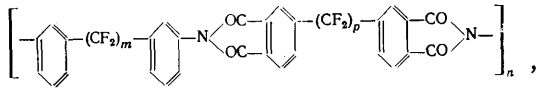
derivatives of αω-diphenylperfluoroalkanes in two ways—by a two-stage synthesis [33,57-59,109] and by polycondensation in the melt [33,58]:



Thus reaction of αω-di-(*m*-aminophenyl)perfluoroalkanes with pyromellitic dianhydride [57,109] and also of di-(*m*-aminophenyl) [33,58] and di-(*p*-aminophenyl) ethers [33,58,59] with the dianhydride of 1,3-di-(3′,4′-dicarboxyphenyl)perfluoropropane in dimethylacetamide yielded polyamides which were then cyclised to the corresponding polyimides either by heat treatment or by treatment with a mixture of acetic anhydride and pyridine [33,57,58,109]. The polyimides based on pyromellitic dianhydride are soluble only in concentrated nitric acid ($d = 1.5$), probably with decomposition ($\eta\log \simeq 0.3$); the polymers based on di(aminophenyl) ethers are sparingly soluble in dimethylacetamide ($\eta_{inh} = 0.56$ and 1.31 for *m*- and *p*-derivatives respectively), their softening temperatures lying in the range 190–240°C.

The variation of the glass temperature with the composition of the copolymers of di-(*p*-aminophenyl) ether with pyromellitic dianhydride and the dianhydride of 1,3-di-(3′,4′-dicarboxyphenyl)perfluoropropane has been investigated [59].

Polyimides containing fluorine atoms in both components ($\eta_{inh} = 0.5–1.7$, $M > 30\,000$),



where $m = 3$ or 5 and $p = 3$, 4, or 7, have been synthesised by the polycondensation in the melt of αω-di-(*m*-aminophenyl)perfluoroalkanes with the dianhydrides of αω-di-(3′,4′-dicarboxyphenyl)perfluoroalkanes [33,58]. The ready solubility of these polyimides in amide solvents and in chlorinated hydrocarbons and also the comparatively low softening temperatures (135–180°C), above which they behave as elastomers, are noteworthy.

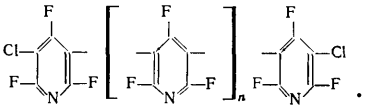
Polybenzoxazoles and polyimides form strong sheets [57,58].

Polyazoles based on derivatives of αω-diphenylperfluoroalkanes begin to decompose in air at about 350 to 400°C [57] (data derived from dynamic thermogravimetric analysis) and are thus somewhat inferior in their thermal stability in air to aromatic polyazoles.

All the above data show that the synthesis of aromatic polyperfluoroalkyleneazoles from derivatives of αω-diphenylperfluoroalkanes with different functional groups is the most general method for the preparation of linear high-molecular-weight polyperfluoroalkyleneazoles containing perfluoromethylene units in the main chain.

There exists also patent data concerning the synthesis of polyimides [60] and poly-1,3,4-oxadiazoles [63] with hexafluoropropyldiene bridges by a two-stage method. Polyazoles fluorinated in both components are distinguished by an unusually high solubility while retaining a high thermal stability: $T_{decomp} \simeq 460–475$°C; T_g (polyimide) ≃ ≃ 340°C.

Brief reports have been published recently on the use of aromatic polyfluoro-derivatives for the synthesis of fluorine-containing polyazoles. Thus poly-1,3,4-oxadiazole has been obtained from the dichloride of tetrafluoroterephthalic acid [35]. A patent [110] (see also Dine-Hart and Wright [54]) describes a synthesis of polypyromellitimides from *m*- and *p*-tetrafluorophenylenediamines, octafluorobenzidine, and pyromellitic dianhydride. Articles made from these polymers can be used for a long time at high temperatures. Polyperfluoropyridine ($n = 15–16$) has been obtained as a solid with m.p. 180–190°C by heating 3,5-dichlorotrifluoropyridine in dimethylformamide in the presence of activated copper [111]:

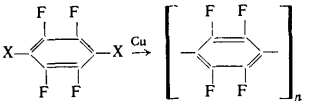


The above data on fluorinated polyazoles evidently show that studies not only on triazine polymers but also on other polyazoles are being vigorously pursued.

V. FLUORINE-CONTAINING POLYPHENYLENE POLYMERS

1. Polyphenylenes

A low-molecular-weight polyperfluoro-*p*-phenylene ($M \simeq 1700$, $T_{soft} > 360$°C) was first obtained in 1955 [112] by the Ullmann reaction in which 1,4-dibromo- or 1,4-di-iodo-tetrafluorobenzene was heated with activated copper powder. The use of 1,4-dichlorotetrafluorobenzene in this reaction leads to the same results [113]:



where X = Cl, Br, or I.

A polyperfluoro-*p*-phenylene with a relatively high molecular weight was synthesised by the decomposition of pentafluorophenylmagnesium bromide in boiling tetrahydrofuran (THF), the properties of the polymers formed depending on the temperature at which the initial organomagnesium compound had been obtained [114,115]. Thus if the latter was obtained at −30°C, a soluble polymer with $M \simeq 15\,000$ is formed, while the organomagnesium compound obtained at a higher temperature yields mainly an insoluble polymer. An insoluble polyperfluorophenylene infusible up to 360°C has also been obtained by the decomposition of pentafluorophenylmagnesium chloride [114,116]:

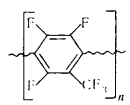
The predominantly *p*-phenylene structure of the polymer was confirmed by the isolation of perfluoroquaterphenyl from the reaction products [114]. A method for the preparation of polyperfluorophenylenes, probably with a *p*-phenylene structure, by decomposing perfluorophenylmagnesium

chloride in boiling tetrahydrofuran in the presence of decafluorobiphenyl, has been suggested in a patent [117]. In the presence of a tenfold excess of the organomagnesium compound, a polyphenylene with a degree of polymerisation of about 25 is obtained.

It is noteworthy that attempts to achieve the synthesis of a polyphenylene by the polycondensation of 1,4-dibromo- and 1,4-di-iodo-tetrafluorobenzene in the presence of sodium or zinc [112] and also by the decomposition of organolithium and organomagnesium compounds derived from 1,4-dibromo- and 4-bromo-tetrafluorobenzene [114] did not lead even to low-molecular-weight polymers of this type.

Polyperfluoro-*m*-phenylene was synthesised simultaneously by a number of workers [114,117-119] by heating 1,3-dibromo- or 1,3-dichlorotetrafluorobenzene with activated copper in decafluorobiphenyl or dimethylformamide and also in the absence of solvents; the reaction with the 1,3-dibromo-derivative leads to the formation of a polymer with a much higher molecular weight (up to about 16 000, $T_{soft} \simeq 300°C$) and requires lower temperatures. Polyperfluoro-*m*-phenylene is more soluble and melts at a lower temperature than polyperfluoro-*p*-phenylene. It is interesting that their thermal stabilities are approximately the same. According to Thrower and White [118], polyperfluoro-*m*-phenylene may prove to be more readily available than its non-fluorinated analogue because of the high reactivity of 1,3-dibromotetrafluorobenzene.

Low-molecular-weight polyperfluorophenylenes ($M \simeq 1500$, $T_{soft} \simeq 200°C$) containing simultaneously 1,3- and 1,4-phenylene units have also been described. They are obtained by the reaction of 1,3-tetrafluorophenylene-dimagnesium dibromide with decafluorobiphenyl (in molar proportions of 2 : 1) in boiling tetrahydrofuran [114]. High-molecular-weight polyperfluorotolylenes,



(M up to 200 000), have been synthesised by the decomposition of 2-heptafluorotolylmagnesium chloride in boiling tetrahydrofuran. They do not melt up to 300°C and their solubility in organic solvents is much higher than that of polyperfluorophenylenes [62,114,120].

High-molecular-weight polyperfluorophenylenes, like polyperfluorotolylenes, are stable in a vacuum up to about 600°C: under the conditions of oxidative degradation, they are less stable and begin to decompose vigorously at about 400°C. The thermal stability of polyperfluorophenylenes *in vacuo* is comparable with that of non-fluorinated polyphenylenes and poly(phenylene oxides), but is lower than the thermal stability of polytetrafluoroethylene.

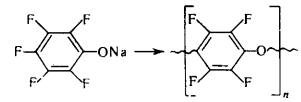
The resistance of polyperfluorophenylenes to thermo-oxidative degradation is inferior to that of the above polymers [62,114,115,121].

It has been noted that, when polyperfluorophenylenes are heated initially in a vacuum at 400°C, their resistance to oxidative degradation is greatly improved.

2. Polyphenylenes with Bridging Groups

Since polyperfluorophenylenes are fairly rigid systems, attempts have been made to improve their flexibility by introducing various atoms or groups of atoms, such as O, S, OCF_2, and others, between the phenyl rings.

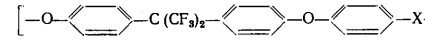
a. Polyoxy(phenylenes). Polyoxy(perfluorophenylenes) were first obtained in 1958 by the thermal decomposition of alkali metal pentafluorophenoxides [122,123]:



According to Pummer and Wall [123], the polymers are formed as a result of nucleophilic attack on the carbon atom adjacent to the fluorine atom by the growing phenoxide anion and they probably contain both 1,3- and 1,4-phenylene units.

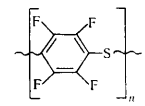
The decomposition of pentafluorophenoxides is carried out in three ways: in the absence of solvents, in an aqueous medium, and in pentafluorophenol [123]. In the first two cases low-molecular-weight polymers are formed. A high-molecular-weight polymer ($M \simeq 12\,500$) has been obtained by heating an excess of sodium pentafluorophenoxide with pentafluorophenol. Polyoxy(perfluorophenylene) is a low-melting vitreous material ($T_{soft} > > 100°C$) soluble in the usual organic solvents: on heating *in vacuo* (260°C, 18 h), it becomes insoluble and acquires rubberlike properties in the temperature range 90 to 300°C. [114] Polyoxy(perfluorophenylene) is much less stable than its non-fluorinated analogue and polyperfluorophenylenes: on heating *in vacuo* for 30 min at 400°C it loses about 47–50% of its weight [114].

Aromatic polyesters with perfluoroisopropylidene units,



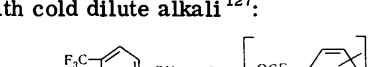
where (I) X = SO_2, T_g = 205°C, and T_f = 255°C and (II) X = CO and T_g = 175°C, have been obtained by the polycondensation of alkali metal phenoxide derivatives of 2,2-di-(*p*-hydroxyphenyl)perfluoropropane with di-(4-fluorophenyl) sulphone or 4,4'-difluorobenzophenone in aprotic solvents at 130–140°C. [124]

b. Polythioperfluorophenylenes. Low-molecular-weight polythioperfluorophenylenes,



have been synthesised in two ways [125]: by the reaction of hexafluorobenzene with sodium sulphide (the polymer has the 1,4-structure with a degree of polymerisation of about 10) and by the thermal decomposition of sodium pentafluorophenoxide. In contrast to polyoxyperfluorophenylene, polythioperfluorophenylene is insoluble in the usual organic solvents and does not melt up to about 300°C. [114] The thermal stability of polythioperfluorophenylene is lower than that of polythiophenylene. It begins to decompose vigorously below 400°C under the conditions of both thermal and thermo-oxidative degradation: the formation of a large residue indicates a significant role of chain-transfer reactions [126].

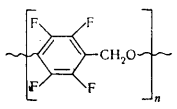
c. Polyoxybenzylenes and polythiobenzylenes. Poly-*o*- and poly-*p*-oxy-$\alpha\alpha$-difluorobenzylenes were first obtained by heating *o*- and *p*-trifluoromethylphenols with cold dilute alkali [127]:



According to the authors, this reaction proceeds via pseudoquinonoid structures, since *m*-trifluoromethylphenol, which is incapable of forming structures of this kind, is resistant to the action of aqueous alkali.

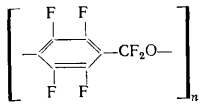
Poly-*p*-oxy-$\alpha\alpha$-difluorobenzylene has also been synthesised by the thermal dehydrofluorination of *p*-trifluoromethylphenol *in vacuo* at 900–950°C, the polymer being formed on the surface of a cold trap in the form of a weakly coloured film [128]. Poly-*p*-oxy-$\alpha\alpha$-difluorobenzylene is sparingly soluble in the usual organic solvents and is resistant to the action of concentrated alkalis.

Poly-oxy-2,3,5,6-tetrafluorobenzylene,



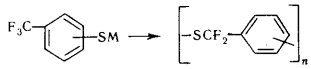
synthesised by refluxing 2,3,4,5,6-pentafluorobenzyl alcohol of 2,3,4,5,6-pentafluorobenzyl bromide with aqueous potassium hydroxide, has been described [129,130]; its melting point is 180–190°C. [130]

A third example of fluorine-containing polyoxybenzylenes is poly-*p*-oxy-perfluorobenzylene:



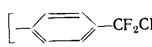
which was synthesised by a number of investigators by heating heptafluoro-*p*-cresol with aqueous bases at 100°C. [114,131,132] Later polyoxyperfluorobenzylene was obtained by the thermal dehydrofluorination of heptafluoro-*p*-cresol *in vacuo*. [128] The mechanism of the formation of the polymer was not elucidated by the authors. The maximum molecular weight of polyoxyperfluorobenzylene is about 3000–5000; it is soluble in the usual organic solvents and its softening temperature varies in the range 65–120°C depending on the molecular weight. Like polyoxyperfluorophenylene, polyoxyperfluorobenzylene gives rise on heating *in vacuo* at about 200°C to a polymer with elastic properties at temperatures above 100°C. The thermal stability of polyoxyperfluorobenzylene is approximately the same as that of polyoxyperfluorophenylene: the weight loss at 350°C in 1 h is 89%.

A method for the preparation of poly-*m*- and poly-*p*-thio-$\alpha\alpha$-difluorobenzylenes has been patented:



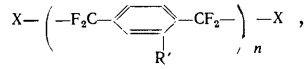
It involves heating Group I metal *m*- or *p*-($\alpha\alpha\alpha$-trifluoromethyl)thiophenoxides at 200°C for 5 days; the reaction may be carried out in pyridine solution. Poly-*m*-thiodifluorobenzylene (degree of polymerisation 12) melts at 285–310°C. [133]

d. Poly-*p*-xylylenes. Poly-$\alpha\alpha\alpha'\alpha'$-tetrafluoroxylylene,

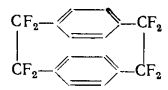


was first synthesised by the pyrolysis of $\alpha\alpha$-dibromo-$\alpha\alpha\alpha'\alpha'$-tetrafluoro-*p*-xylylene in a vacuum at 330°C in the presence of zinc in the form of an amorphous film on the surface of a trap cooled to −78°C; the conversion of the initial monomer into the polymer is about 8% and the softening temperature of the polymer is 380°C. The authors suggest that $\alpha\alpha\alpha\alpha$-tetrafluoro-*p*-quinodimethane, which is stable in the gas phase but polymerises rapidly in the liquid phase, is an intermediate in the reaction [134]. Other investigators believe [135] that the reaction can also proceed via the free biradicals $F_2CC_6H_4CF_2$.

High-temperature vacuum pyrolysis (700–950°C) of dihalides [136,137] and disulphones of the type [136,137],



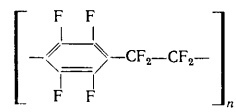
where $n = 1$ or 2, X = Cl, Br, or SO_2R (R is a small alkyl group), and R′ = H, Cl, or C_6H_5, and also of the cyclic dimer of $\alpha\alpha\alpha'\alpha'$-tetrafluoroxylylene [136,138],



has been recently used successfully in the synthesis of poly-$\alpha\alpha\alpha'\alpha'$-tetrafluoro-*p*-xylylenes. Strong transparent sheets have been obtained by this method from the disulphones and the dimer.

Poly-$\alpha\alpha\alpha'\alpha'$-tetrafluoroxylylene (m.p. about 500°C) is a highly crystalline insoluble polymer with a very high thermal stability; the mechanical properties of sheets of this polymer hardly change on heating in air for 3000 h at 250°C or 100 h at 300°C.

A method for the preparation of polyperfluoro-*p*-xylylene from the corresponding disulphone has also been patented [137]:



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The new field of the chemistry of organofluorine compounds (polycondensation fluoropolymers) discussed in the present review is at present in the stage of establishment and development, the number of studies in this field increasing continuously: for example three-quarters of the relevant studies were published in the 1960's.

The interest in polycondensation fluoropolymers can be readily understood: in almost every class materials have been found with promising operational properties (high thermal stability, chemical stability, elasticity at low temperatures, etc.). Thus polyperfluoroalkylenetriazines have the highest thermal stability among the known elastomers, poly(hexafluoropentylene adipate) has found application in the preparation of special oil- and frost-resistant rubber, fluorine-containing polyurethanes based on polyperfluoroethers can be used as elastomers at low temperatures, etc.

At the same time one should note that the introduction of fluorine atoms does not always lead to the improvement of the properties of the polymer and in some cases a decrease of thermal and chemical stability, for example, has been observed as a function of the structure of the polymer. Unfortunately exhaustive data on the properties of polycondensation fluoropolymers are frequently lacking in the literature and therefore it is difficult to make a comparative analysis of fluoropolymers and their non-fluorinated analogues. Whenever possible, such a comparison has been made in the appropriate places in the text.

Polycondensation reactions of fluorine-containing compounds frequently lead to polymers with a lower molecular weight compared with their non-fluorinated analogues. This is due to the powerful electron-accepting influence of the fluorine atoms on the reactivity of the functional

groups. Recently definite progress has been achieved in the synthesis of polycondensation fluoropolymers—high-molecular-weight compounds of various classes which were previously regarded as unattainable—had been synthesised. Their synthesis became possible owing to the application of new methods of polycondensation and also the use of new types of fluorine-containing monomers.

The entire accumulated experience on the synthesis of fluoropolymers and the study of their properties show that further studies in this interesting series of still new polymers are justified.

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The Photoelectric Effect at the Metal-Electrolyte Boundary

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Photoelectrochemistry is a new branch of physical chemistry, with many applications in the study of boundary layer structure, the energetics of electrons in solutions, the mechanism of photoemission, and the kinetics of fast reactions in solutions initiated by solvated electrons. 110 references.

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I. INTRODUCTION

The generation of photocurrents by illumination of the interface between an electrode and an electrolyte solution was first reported by Becquerel over 100 years ago[1]. However, the elementary acts involved in the electrode photoeffect have only recently been characterised by work done at Harwell (England)[2-4] and at the Chemical Physics and the Electrochemistry Institutes of the USSR Academy of Sciences[5-11].

According to current views, the following charge separation processes have to be considered when a metal-solution interface is illuminated: 1) photoemission of electrons from the metal into the electrolyte solution; 2) photoionisation of the surface donor-acceptor complexes which include the electrode as one component; 3) electrode reactions involving metastable species produced by the interaction of photoemitted electrons with the molecules of the medium; 4) electrode reactions involving the products of photochemical reactions in solution.

In real systems these processes usually overlap, and complicated experimental procedures are needed to resolve them.

This review is concerned with elementary, light-induced charge transfer processes at the metal-electrolyte boundary: a) in solutions which do not absorb in the spectral region used to excite the electrode, and b) in solutions of photochemically active redox systems, including a light-absorbing dye.

The electrode photoeffect has great theoretical and practical interest. Photo-emission from metals into electrolyte solutions offers a new approach to the study of the behaviour of low-energy electrons in condensed media. Its characteristics are directly determined by the structure of the interfacial boundary layer and by the physicochemical properties of the solution.

The photoelectrochemical method of detecting unstable species in solution is much more sensitive than alternative methods such as optical and radiation methods.

II. EXPERIMENTAL METHODS

The electrode photoeffect can be studied by three methods: with constant illumination, interrupted illumination, and pulse illumination. The relaxation methods are by far the more important, because they give both the magnitude and the kinetic constants of the photoeffect.

The photocurrent in an electrochemical cell exposed to steady light can be measured with a sensitive galvanometer[11] or a polarograph[13]. The success of the method depends on the purity of the reagents, since it is essential to avoid significant Faradaic currents in this work. Intermittent photocurrent is obtained by modulating the light supplied to the electrode. Barker[3] used a square-wave polarograph to measure intermittent photocurrents (f = 225 Hz). For sinusoidal modulation, the measuring equipment consists of a narrow-band amplifier tuned to the modulation frequency, followed by a synchronous detector[10]. The current-voltage curve for the photoeffect is plotted directly, by sweeping the voltage (Figs. 1 and 2). An apparatus has been described[14] in which the impedance of an electrochemical cell can be measured by sinusoidally modulating the illumination or by applying a small alternating voltage. The measurements of the components of the photoimpedance, proposed by Rotenberg and coworkers[15], has not yet been realised experimentally.

The pulse method was first applied by Berg[16]. One form[8] of the apparatus is shown in Fig. 3. The photopotential which appears across a standard resistor in series with the cell is displayed on a double-beam oscilloscope. The second channel of the oscilloscope is used to record the wave-form of the light pulse (Fig. 4).

Powerful light pulses in the visible and the ultraviolet region of the spectrum are obtained by means of mercury or xenon lamps. Lasers also are a convenient source of radiation[9,17].

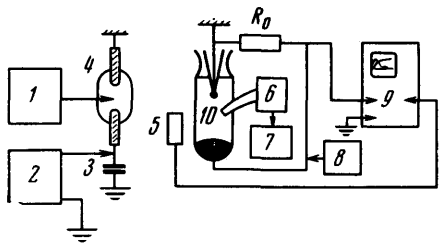

Figure 1. Pulse apparatus: *1*) firing circuit; *2*) condenser charging circuit; *3*) pulse condenser; *4*) flash lamp; *5*) synchronising photodiode; *6*) reference electrode; *7*) potentiometer for the working electrode; *8*) commutator circuit for measuring the capacity of the working electrode; *9*) oscilloscope; *10*) polarographic cell; R_0 is the standard resistor.

An analysis of the equivalent circuit of the cell shows that the measured signal $V_{ph}(t)$ is related to the photocurrent $I_{ph}(t)$ flowing through the interface by the expression

$$V_{ph}(t) = \exp(-t/RC) \int_0^t 1/C I_{ph}(t') \exp(t'/RC)\, dt' \qquad (1)$$

where t is time, R is the resistance of the circuit, and C is the capacity of the electrical double layer (~16 μF cm^{-2}).

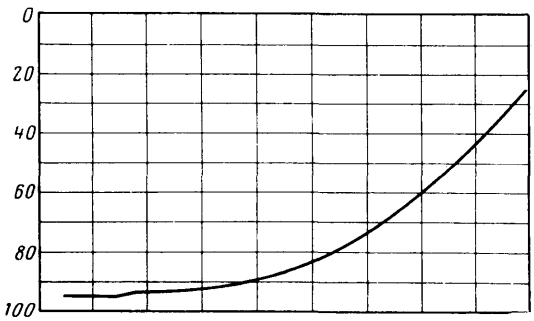

Figure 2. Plot of the photocurrent obtained by sweeping the potential. The potential is plotted horizontally and the photocurrent vertically.

For pulse measurements the standard resistance is chosen to give an RC value much greater than the duration of the pulse of photocurrent. In this case, $V_{ph}(t) = \int_0^t C^{-1} \cdot I_{ph}(t')dt'$, i.e. the measured photopotential is proportional to the charge transferred across the interface. With the dropping mercury electrode—a very convenient photocathode—the condition is satisfied by taking $R \geq 10^5$ ohm for pulse durations of 10^{-5}–10^{-3} s. The capacity, which must be known in order to calculate the charge, is measured by the commutator method[18].

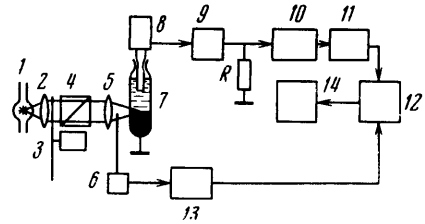

Figure 3. Apparatus for intermittent illumination: *1*) DRSh-1000 lamp; *2*) quartz lens; *3*) chopper; *4*) Glan Nicol prism; *5*) quartz condenser; *6*) photodiode; *7*) photocathode; *8*) polarisable reference electrode; *9*) polarising circuit; *10*), *11*), *13*) V6-2 amplifiers; *12*) KZ-2 synchronous detector; *14*) chart recorder.

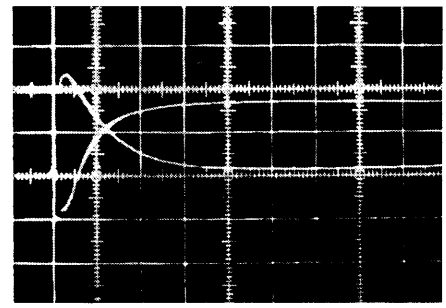

Figure 4. Oscillograms of the photoemission signal $V(t)$ (upper trace) and of the light pulse $L(t)$ (lower trace). Calibration: 200 μs cm^{-1} (horizontal axis) and 1 mV cm^{-1} (vertical axis).

In Delahay's differential method[19], the potential difference between two identical electrodes (one of which is kept in the dark while the other is exposed to a pulse of light) is measured. With modulated or steady illumination one usually measures the quantity $V_{ph}(t) = I_{ph}(t) \cdot R$. This regime corresponds to the condition $\omega_M RC \ll 1$, where ω_M is the modulation frequency. For a dropping electrode this condition is satisfied by $R \leq 500$ ohm and $\omega_M \leq 10^3$ Hz. An analysis of the measurement errors[20] has shown that in the steady illumination regime the error is usually 3–4%, as compared with 7–8% for pulses of 10^{-6}–10^{-7} s duration. The precision of the pulse method can be increased by using storage oscilloscopes and amplitude–time analysers for the microsecond range[21]. Stroboscopic light sources, including

pulsed gas lasers, are very important in studies of the relaxation phenomena associated with photoemission. They are used in conjunction with signal averaging devices [22].

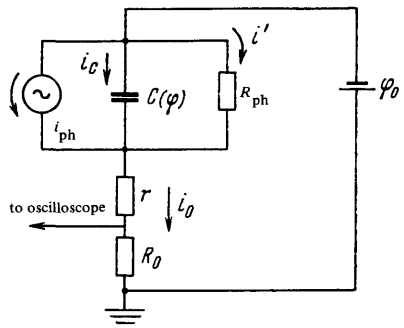

Figure 5. Equivalent circuit of the electrochemical cell during the passage of photocurrent.

Korshunov and coworkers [22] illuminated the electrode–solution interface with pulses from a nitrogen laser ($\lambda = 3371$ Å) of 20 ns duration at the 0.35 level. The time resolution of the apparatus was 10 ns. In order to avoid the slow ($10^{-7}-10^{-5}$ s) signal fluctuations due to electrocapillary effects, the dropping mercury electrode was replaced by an amalgamated gold wire ($s = 2.5 \times 10^{-3}$ cm^2). In order to match the signal to the input of the measuring apparatus, a standard resistance of 150 ohm was used. The time constant of the integrating circuit ($\sim 2 \times 10^{-5}$ s) allowed processes occurring over periods of $10^{-8}-10^{-5}$ s to be studied. The repetition frequency of the laser pulses was 50 Hz.

III. GENERAL ASPECTS OF PHOTOEMISSION INTO ELECTROLYTE SOLUTIONS AND IONISATION OF SURFACE DONOR–ACCEPTOR COMPLEXES

The concepts of cathodic photocurrent due to u.v. illumination of solutions of indifferent electrolytes, and of the emission of electrons from an electrode into a solution, are both due to Barker [2]. Earlier, pioneering work on the electrode photoeffect includes Heyrovsky's hypothesis [23-27] of the surface donor–acceptor complex and Berg's "hot electrode" concept [28-33]. Heyrovsky considered that the photocurrent is produced by ionisation of a surface donor–acceptor complex, consisting of the electrode on the one hand and the solvent or solute on the other hand. Absorption of a light quantum raises the complex to an excited state. The direction of the electron transfer (i.e. the sign of the photocurrent) depends on the relative positions of the energy levels of the complex, the energy level of the electrode being determined by the electrode potential φ. Heyrovsky's hypothesis was based on the observation of anodic photocurrents at $\varphi > \varphi_{z.c.}$, where $\varphi_{z.c.}$ is the potential at the point of zero charge, in solutions of organic molecules containing the functional group $-\underset{\underset{O}{\|}}{C}-\underset{\underset{X}{|}}{C}=$.

The formation of surface donor–acceptor complexes has since been confirmed for a number of compounds, but only at $\varphi > \varphi_{z.c.}$ [10].

According to Berg, the photoexcitation of electrons in the metal causes the electrolyte ions to be discharged at more positive potentials. The suggestion had been put forward earlier by Bowden [34], who had observed a decrease of hydrogen overvoltage at an illuminated electrode. However, since the relaxation time of the charge in the metal [35] is less than 10^{-16} s, this mechanism cannot be accepted.

Barker based his hypothesis on a detailed study of the spectral and current–voltage characteristics of the electrode photoeffect, because properties such as proportionality to the light intensity, short persistence, and the presence of a long-wave threshold can be explained by almost any model. We shall discuss the problem in some detail in the following paragraphs.

Photoemission from metals into electrolyte solutions can be treated as three distinct steps: a) interaction of a photon with the conduction electrons of the metal, causing an electron to pass through the potential barrier at the interface; b) thermalisation and solvation of the emitted electron in the solution medium; c) chemical and electrode reactions of the solvated electron, and of the products of its interaction with acceptor molecules present in solution.

The first step in photoemission is quite different from photoemission into a vacuum, because of the sharp drop in potential across the electrical double layer over distances of 10 Å or less (in concentrated solutions), and because of the Coulombic screening of the emitted electron with respect to the image forces.

The double layer at the interface affects the emission properties of the metal electrode, because the emitted electrons can tunnel through the dense part of the double layer, thus lowering the work function of the metal by an amount equal to the applied potential. The screening effect operates on the positive charge in the metal electrode produced by the emission of an electron, and is due to the ions in the electrical double layer. (The electron in the solution is screened much more slowly). According to Brodskii and Gurevich [6], this effect should result in the replacement of Fowler's parabolic law [36,37] by a "five-over-two" law of the form

$$I_0 = L\chi(\omega)(h\omega - h\omega_0 - e\varphi)^{5/2} \qquad (2)$$

where L is the light intensity, $\chi(\omega)$ is a function of the properties of the metal and of conditions of light absorption, h is Planck's constant, ω is the frequency of the incident light, ω_0 is the frequency of the long-wave limit of the photoeffect, e is the electronic charge, and φ is the potential of the electrode relative to the potential at the point of zero charge.

The second step in photoemission is the least well understood at the moment, because very little is known about the differential scattering cross-sections of low-energy electrons (0.5–3 eV) in condensed media. If we assume that the main scattering mechanism in water is dipole relaxation, the characteristic thermalisation time works out [38] to $10^{-12}-10^{-13}$ s. The time for the hydration of an electron, i.e. the time needed to convert it into a polaron state, is [38] $\sim 10^{-12}$ s.

The third step in photoemission concerns the behaviour of the electrons after thermalisation and hydration. Such electrons can be captured by acceptors in solution, or they can return to the electrode. The capture of a solvated electron by an acceptor is diffusion-controlled,

with a characteristic time of $10^{-6}-10^{-9}$ s depending on the concentration of the acceptor. The molecule containing a trapped electron can itself undergo homogeneous or heterogeneous (electrode) reactions; furthermore, the homogeneous reaction product can undergo further reaction at the electrode. Thus, the experimentally observed photocurrent depends, in general, on the emission current I_0, the diffusion current of electrons returning from the solution I_1, and the currents (I_{2i}) due to the electrode reactions of the species produced from the acceptor containing a trapped electron:

$$I = I_0 - I_1 + \sum_i I_{2i}$$

Various electron acceptors are added to the solution in order to minimise the reverse diffusion current I_1: these can be neutral (N_2O, CO, acrylonitrile), positively charged (H^+), or negatively charged (NO_3^-, NO_2^-, BrO_3^-, CN^-, SeO_3^-, TeO_4^-, etc.) [2,27].

Barker solved the steady-state problem for the simplest case (no side reactions) by the equivalent circuit method[3]. Sinusoidally modulated[39] and pulsed[20] illumination were treated separately. Solution of the non-stationary diffusion equation gives the following expression for the photocurrent produced by illumination for times longer than the times involved in the reverse current of solvated electrons and in electron capture by the acceptors (estimated to be less than 10^{-6} s):

$$I = L(t)\int_0^\infty f(x)\left\{1-\exp\left(-\sqrt{\frac{kc}{D_s}}\,x\right)\right\}dx \qquad (3)$$

Under these conditions, $I_0 = L(t)\int_0^\infty f(x)dx$, where $L(t)$ is the intensity of the exciting light, $f(x)$ is a function of the source of solvated electrons, x is the distance from the electrode, k is the rate constant of the reaction between the solvated electron and an acceptor molecule, c is the acceptor concentration, and D_S is the diffusion coefficient of the solvated electron.

In real systems, the emission current usually includes a component from the electrode reactions of the electron–acceptor complexes, and also of the products of their transformations in solution. These effects can distort the $I(\varphi)$ current–voltage characteristic, since the rate constant of the electrode reaction is (in general) a function of φ. However, if the electrode reactions of the products do not depend on φ in the region of interest, the current–voltage characteristic $I(\varphi)$ will be determined by $I_0(\varphi)$ and by the potential dependence of the source of solvated electrons.

This situation occurs for the acceptors N_2O and H_3O^+ (and for protons at $\varphi < -0.6$ V†), when the transfer of the second electron at the electrode–electrolyte interface involves the reduction of a hydroxyl radical or atomic hydrogen, and the emission current is simply doubled:

$$\begin{cases} N_2O + e_s^- \rightarrow N_2O^- \\ N_2O^- + H_2O \rightarrow N_2 + OH + OH^- \end{cases}$$

$$\begin{cases} H_3O^+ + e_s^- \rightarrow H + H_2O \\ H_{ad} + H_2O + e \rightarrow H_2 + OH^-, \end{cases}$$

where e_s is a solvated electron. N_2O and H_3O^+ have been used to investigate the detailed aspects of photoemission in solutions of electrolytes.

Some of the early workers[40,41], and also Heyrovsky[27], plotted their current–voltage and spectral measurements of the electrode photoeffect using ($\lg Q$, φ) and ($\lg Q$, $\hbar\omega$) co-ordinates, but Barker[3] and Delahay[17], who did not distinguish between photoemission into a vacuum and into a solution of electrolyte, used ($Q^{1/2}$, φ) and ($Q^{1/2}$, $\hbar\omega$) co-ordinates. (Here Q is the emitted charge). In both cases, the experimental results lay on a straight line over a limited region of potential. A more general law—the "five-over-two" law was first proposed[8,20] for the photoemission from mercury in the wave-length region 250–450 nm at potentials up to −0.7 V (relative to the point of zero charge) in acid solutions and up to −1.5 V (z.c.) in neutral or alkaline solutions containing nitrous oxide as an acceptor. It was shown that the current–voltage characteristics of the photoeffect "straighten out" when plotted in ($Q^{0.4}$, φ) co-ordinates‡ (Fig. 6). For solutions with different acceptor concentrations but constant ionic strength the straight lines intersect at one point on the potential axis.

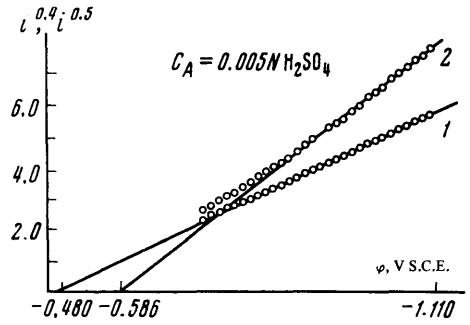

Figure 6. Current–voltage characteristic of the photoeffect in 0.005 N H_2SO_4 + 0.495 N K_2SO_4; λ = 405 nm: *1*) $i^{0.4}$ against φ; *2*) $i^{0.5}$ against φ.

Other workers[11,42] have also reported "linearisation" of the voltage–current characteristics for the photoemission effect on ($I^{0.4}$, φ) or ($Q^{0.4}$, φ) co-ordinates. The spectral dependence of the photoeffect gives a reasonably good straight line when plotted as $Q^{0.4}$ against $\hbar\omega$ (Fig. 7). The current–voltage curves for different $\hbar\omega$ values intersect the potential axis to give increments ($\Delta e\varphi$) proportional to the change in the energy of the light quantum ($\Delta\hbar\omega$), the proportionality coefficient being unity. Barker[3] finds the same value for the ratio $\Delta\hbar\omega/\Delta e\varphi$: the values between 2 and 3 reported by Heyrovsky[27] are probably due to secondary reactions which were ignored.

† Throughout this review, potentials are quoted relative to the saturated calomel electrode unless accompanied by a statement to the contrary.

‡ Reported deviations[22] from Eqn. (2) in the threshold region (at 436–579 nm) are probably due to thermal excitation processes in the metal, producing a photocurrent larger than required by Eqn. (2). The form of the threshold factor for $\frac{\hbar\omega - \hbar\omega_0 - e\varphi}{kT} \simeq 1$ is given in Ref. 6.

This means that the transmission coefficient of the barrier is sensibly constant within the dense part of the electrical double layer, which confirms the initial assumption of the Brodskii–Gurevich theory that the red photoemission threshold is linearly related to the electrode potential. Experiments on the frequency dependence of the photoemission by varying $e\varphi$ and $\hbar\omega$ together in such a way that the energy of the emitted electrons ($\hbar\omega - \hbar\omega_0 - e\varphi$) remains constant have shown that the function $\chi(\omega)$ in Eqn. (2) is independent of the medium into which photoemission occurs and is determined by the light absorption law in the metal. This experiment is not applicable to photoemission into a vacuum because of the frequency dependence of the threshold factor. The function $\chi(\omega)$ is found[22] to be a cubic hyperbola (Fig. 8): $\chi \sim \frac{1}{\omega^3}$. This result is consistent with the theory of photoemission assuming that the amplitude E of the light wave vector does not exhibit a singularity at the metal surface.

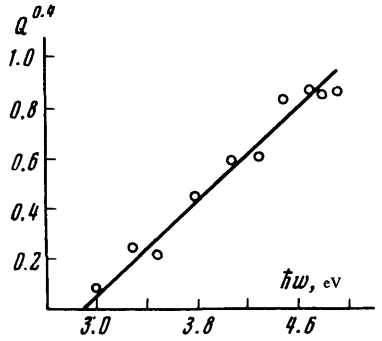

Figure 7. Spectral characteristic of the photoeffect in 0.1 N H_2SO_4; $\varphi = -0.8$ V.

When the energy of the emitted electrons is 1 eV and the energy of the absorbed photons is 3.52 eV, the quantum yield of the photoemission process is $(1.2 \pm 0.3) \times 10^{-4}$. This value agrees with the quantum yield of the photoemission into a vacuum[43] of electrons of 1 eV energy from a metal with a work function of 3.2–3.4 eV.

The work function from mercury into water W_0, calculated from spectral and current–voltage experiments by means of Eqn. (3), is 3.2 ± 0.05 eV (with H_3O^+ as the acceptor) or 3.13 ± 0.05 eV (with N_2O as the acceptor). This is close to the value of W_0 proposed by Frumkin from thermodynamic data[44] and to the "light quantum able to induce photocurrent at the point of zero charge" observed by Heyrovsky[27] with N_2O and H_3O^+ acceptors.

Many acceptors give current–voltage characteristics different from those described above for N_2O and H_3O^+ acceptors. The difference arises because the rate of the electrode reactions involving the products of electron capture by those acceptors varies with the potential[3,45].

We have shown[45] that in the presence of anionic acceptors both the current–voltage curve and the oscillographic $V(t)$ display of the photopotential depend on the Ψ' potential, on the acceptor concentration, and also on the ionic strength and on the pH of the solution. If the chemical reactions of the acceptors containing a captured electron are slow in comparison with the time of illumination, the trace of $V(t)$ does not follow the integral of the flash.

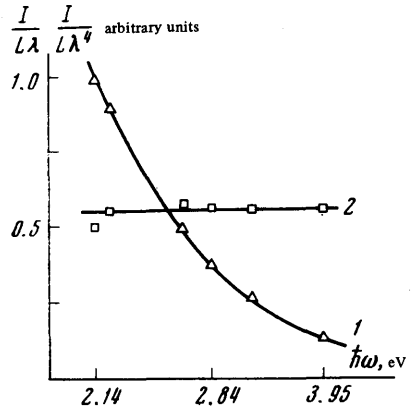

Figure 8. Frequency dependence of the photoemission current from mercury into 0.1 N KCl (acceptor N_2O); *1*) $I/L\lambda$; *2*) $I/L\lambda^4$; λ is the wave-length of the exciting light. Measured at constant $\hbar\omega - \hbar\omega_0 - e\varphi = 0.5$ eV.

Thus, in 1 M solutions of $NaNO_3$, KIO_3, and $K_2C_2O_4$ the current–voltage curves are S-shaped: at the more negative potentials the experimental points lie on straight lines in $Q^{0.4}(\varphi)$ plots, which can be extrapolated to give the shift from 3.2 eV of the threshold potential ($\Delta\varphi_b$).

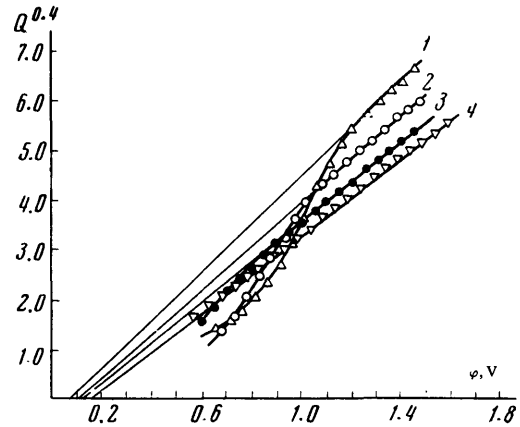

Figure 9. Emitted charge as a function of electrode potential in $NaNO_3$ solutions: *1*) M; *2*) 10^{-1} M; *3*) 10^{-2} M; *4*) 10^{-3} M (λ = 355 nm).

This can be negative ($\Delta\varphi_b = -0.4$ V for $NaNO_3$ and –1.1 V for $K_2C_2O_4$) or positive ($\Delta\varphi_b = 0.5$ V for KIO_3): see Figs. 9, 10, 11. However, when the contribution to the

photocurrent from secondary reactions can be ignored (acceptor concentration $10^{-3}-10^{-4}$ M, or alkaline medium) the function $Q^{0.4}(\varphi)$ becomes linear, and the work function approaches the value 3.2 V. In $K_2C_2O_4$ solutions we find, in addition to a cathodic photocurrent at negative potentials, an anodic photocurrent at $\varphi > \varphi_{z.c.}$, with a vanishingly small photoeffect in the intermediate potential region. KIO_3 solutions are distinguished by the presence of cathodic photocurrent at potentials more positive than the photoemission threshold.

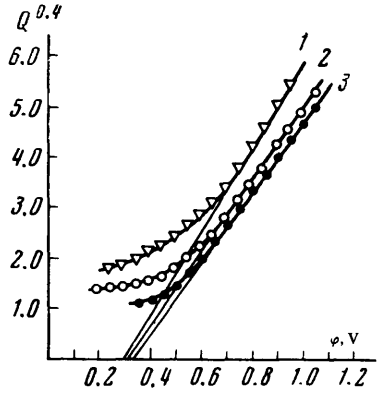

Figure 10. Emitted charge as a function of electrode potential in KIO_3 solutions: *1*) 10^{-1} M; *2*) 10^{-2} M; *3*) 10^{-3} M (λ = 355 nm).

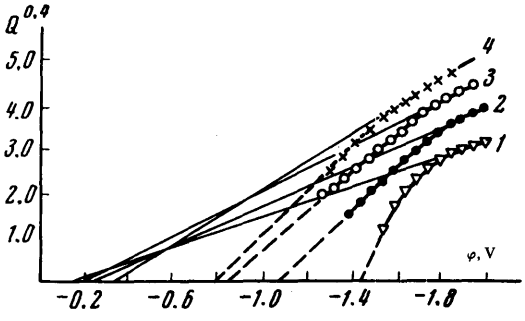

Figure 11. Emitted charge as a function of electrode potential in $K_2C_2O_4$ solutions: *1*) M; *2*) 10^{-1} M; *3*) 10^{-2} M; *4*) 10^{-3} M (λ = 355 nm).

The anodic photocurrent in oxalate solutions, and the cathodic photocurrent in iodate solutions at potentials more positive than the threshold potential, stem from the formation of a surface donor–acceptor complex. This can happen when $\varphi > \varphi_{z.c.}$, when the concentration of IO_3^- and $C_2O_4^{2-}$ in the electrical double layer suddenly increases. The anodic photocurrent is due to light-induced charge transfer to the electrode from the oxalate anion, which has a low ionisation potential, and the cathodic photocurrent to charge transfer (induced by light) from the metal to the iodate anion, which has a high electron affinity.

This conclusion was reached from a study of polarisation selectivity, an important feature of the surface photoeffect. This effect, associated with the polarisation of light absorption in metals, follows from the condition of conservation of momentum, which can be satisfied in the surface photoeffect only in a direction perpendicular to the surface[46]. Conversely, in the photocurrent model involving ionisation of surface complexes, polarisation selectivity seems improbable, since the binding energy of the complex is comparable to the molecular vibration energy, and complex formation leads to the interaction of vibrational states of different symmetry[47].

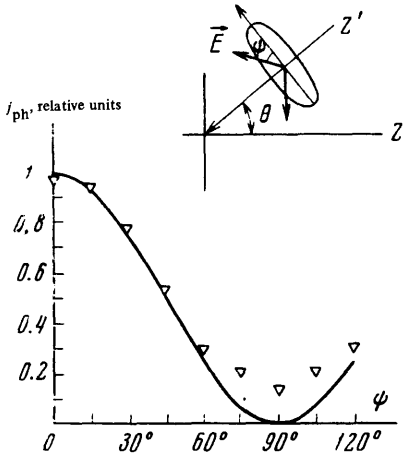

Figure 12. Polarisation dependence of the photoeffect in 0.1 N K_2SO_4 (φ = −1.4 V); z is the direction normal to the electrode surface, θ is the angle of incidence of the light, E is the vector of the electric component of the electromagnetic wave, ψ is the polarisation angle in the incidence plane (z,z'), j_{pH} is the measured photocurrent, the symbol ▽ denotes experimental points, the full line is a plot of $\cos^2\psi$.

Polarisation selectivity of the electrode photoeffect was predicted by Brodskii and Gurevich[6] and experimentally demonstrated by Korshunov and coworkers[10]. A decrease in photocurrent with a decrease in the normal component of the electric vector was observed at negative potentials in all the solutions examined (H_3O^+, N_2O, and anion acceptors). The polarisation ratio varied between 2.5 and 7, depending on the angle of incidence of the light on the photocathode (Fig. 12).

Since for the linear photoeffect $j \sim E_{\parallel}^2 = E_0^2 \sin^2\theta \cos^2\Psi$ (where θ is the angle of incidence, Ψ is the polarisation angle of the electric vector E of the electromagnetic wave in the incidence plane, j is the photocurrent), the angular dependence of the photocurrent is given by

$$j = j_0 \sin^2\theta \cos^2\psi, \qquad (4)$$

which satisfactorily describes the observed polarisation behaviour.

Polarisation of the cathodic photocurrents has been observed also in $H_2C_2O_4$ and $K_2C_2O_4$ solutions, but the

anodic photocurrents in these solutions show practically no polarisation selectivity.

The polarisation selectivity of the cathodic photocurrent is proof that the photoeffect is the result of photoemission of electrons from the metal into the solution. Conversely, the lack of selectivity of the anodic photocurrent can be taken as evidence that the photoeffect at $\varphi > \varphi_{z.c.}$ arises from light-induced electron transfer in the surface complex from the oxalate anion (which has a low ionisation potential) to the metal.

IV. STATUS OF THE "FIVE-OVER-TWO" LAW AND OF THE DISTRIBUTION FUNCTION OF SOLVATED ELECTRONS

The good qualitative and quantitative agreement between the spectral and current–voltage characteristics of the electrode photoeffect and Brodskii and Gurevich's photoemission theory[6] is evidence that we are dealing with an emission phenomenon, but it does not prove that the "five-over-two" law is in any way a fundamental one.

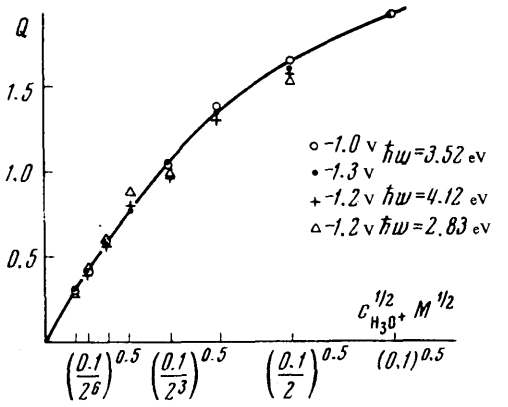

Figure 13. Emitted charge as a function of H_3O^+ acceptor concentration for different φ and $\bar{n}\omega$. The scale of Q is chosen so as to bring into coincidence the points for the maximum acceptor concentration ($c_{H_3O^+} = 0.1\ N$, far right of the curve).

Thus, as already stated, the experimental $I(\varphi)$ and $I(\bar{n}\omega)$ plots are determined not only by the characteristics of the emission current, but also by the dependence upon the energy of the emitted electrons of the distribution function describing the source of solvated electrons. Since the residence time of a solvated electron is much greater than its formation time, the trapping process may be described in terms of an initial distribution of solvated electrons, produced by the photoemission. With this assumption, the variation of the photocurrent (or emitted charge) with acceptor concentration at different photon energies and electrode potentials can be used to arrive at the form of the distribution for different initial electron energies. The charge emitted from mercury into an electrolyte solution under pulse illumination has been studied[48] over a range of concentrations of the electron acceptors H_3O^+, N_2O, and NO_3^-. In the absence of secondary reactions by the electron-filled acceptors, the experimental $Q(c)$ curve is related to the function of the source of solvated electrons $f(x)$ by Eqn. (3).

Fig. 13 shows a plot of $Q(c)$ for H_3O^+ at different values of φ and $\bar{n}\omega$. The arbitrary scale of Q is normalised so as to make the experimental Q values at the maximum acceptor concentration (0.1 M) coincide.

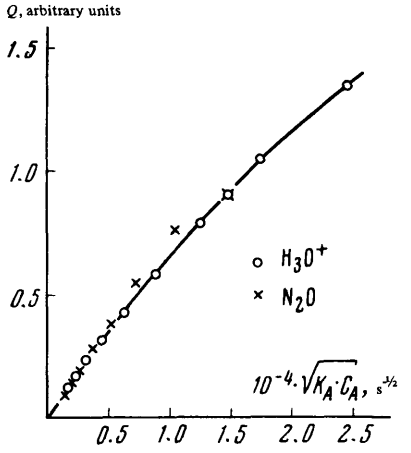

Figure 14. Emitted charge as a function of the parameter $\sqrt{kc}$.

Within experimental error (±5%), the measurements are described by a single curve, i.e. the source function is independent of the emitted electron energy over the range 0.5–1.6 eV. Measurements of Q as a function of the capture efficiency $(\kappa c)^{1/2}$ for different acceptors shows that the source function is also independent of the nature of the acceptor (Fig. 14). From these results we may conclude that the source function is finite at $x = 0$ and can be expressed by the summation

$$f(x) = \sum_i \left(\frac{kc}{D_s}\right)^{1/2} e^{-x/x_{0i}} \qquad (5)$$

Because the experimentally accessible range of $(\frac{kc}{D_s})^{1/2}$ measurements is limited, only the characteristic length x_0 of the distribution can be determined. If the source function is exponential,

$$\frac{Q(c)}{\sqrt{c}} + Q(c)\sqrt{\frac{k}{D_s}}x_0 = Q_0\sqrt{\frac{k}{D_s}}x_0\ , \qquad (6)$$

and a linear relation between $\frac{Q}{\sqrt{c}}$ and Q should be observed.

Eqn. (6) is satisfied at high values of Q, i.e. at high acceptor concentrations. For $D_S = 5 \times 10^{-5}$ cm^2 s^{-1} [3] and $k = 8.7 \times 10^{10}$, the results for H_3O^+ give $x_0 = 16$ Å (Fig. 15).

However, at lower values of Q we observe deviations from linearity: at $c \leqslant 5 \times 10^{-4}$ M for H_3O^+ and at $c < 10^{-3}$ M for NO_3^-. With N_2O ($c_{max} = 2.5 \times 10^{-2}$ M), $Q/\sqrt{c}$ is practically independent of Q. The deviation from linearity of the function $\frac{Q}{\sqrt{c}}(Q)$ may result from a decrease

in the rate constant of the reaction between the solvated electron and the acceptor, as indicated by radiation-chemical data[49,50], or alternatively it may be due to the failure of Eqn. (6) to provide a satisfactory approximation at small values of x. At low acceptor concentrations, when the major contribution to Q comes from the tail of the source distribution function, the observed non-linearity suggests that $f(x)$ falls off more sharply at large values of x than given by Eqn. (6) with $x_0 = 16$ Å.

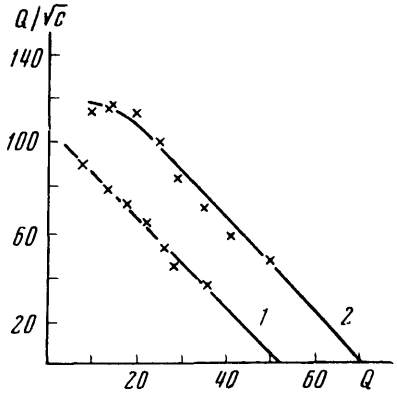

Figure 15. Plots of $Q/\sqrt{c}$ against Q for H_3O^+. Ionic strength held constant (1 N) by adding Na_2SO_4; $\lambda = 300$ nm: *1*) $\varphi = -1.0$ V; *2*) $\varphi = -1.2$ V.

The independence of the source function upon the energy of the emitted electrons in the range $0.5 \leq E \leq 1.5$ eV is also confirmed by the good fit to the "five-over-two" power law of the current–voltage curves at different acceptor concentrations. The results justify the conclusion that the experimentally observed "five-over-two" law has a fundamental significance, i.e. that the Brodskii–Gurevich model[6] of photoemission into a solution is essentially correct. This conclusion is also relevant to the MDM structure (metal–dielectric–metal), for which the photoemission model is similar to the model of photoemission into electrolyte solutions[7], with similar deviations form Fowler's law[51–56].

The escape distance of the electron from the electrode (16 Å for water) is consistent with the mean free path of the secondary electrons produced in the radiolysis of aqueous solutions, for which the values 16 Å and 30 Å have been obtained[57,58] by an analysis of the diffusion kinetics of the radiolysis process.

The value $x_0 = 16$ Å suggests that the main scattering mechanism for low-energy electrons is inelastic interaction. It may be assumed that the energy scattering process involves vibrational relaxation (for water, the relevant vibrational levels are 0.198, 0.474, and 0.488 eV)[59].

As already stated, x_0 has been evaluated on the assumption that the electron becomes solvated before being captured by an acceptor, but the value of x_0 is too small to exclude the possibility of direct capture of unsolvated ("dry") electrons. The diffusion equation holds true if the mean free path, determined by scattering processes (e.g. as a result of vibrations), under equilibrium conditions is larger than the wave packet[60]

$$\lambda = \frac{h}{(3m_0kT)^{1/2}} = 10\ \text{Å} \qquad (7)$$

so that the capture of "dry" electrons by acceptors, followed by release of the electrons to the electrode, can be treated as a diffusion process only at distances greater than λ, whereas x_0 is comparable to λ in magnitude. The relative contribution of solvated and "dry" electron interactions with the acceptor can be evaluated from the kinetics of electron release for irradiation times of the order of the diffusion time of solvated electrons to the electrode (10^{-8}–10^{-9} s).

The kinetics of the photocurrent integral have been studied with a nitrogen laser: in a 1 N H_2SO_4 solution the photocurrent integral is ($\Delta t = 10^{-8}$ s) within experimental error identical with the integral of the light pulse, recorded with a fast photomultiplier. The upper limit of the characteristic length x_0 follows directly from this result: for $\Delta t = 10^{-8}$ s, $x_0 < 70$ Å.

According to Wolf and coworkers[61], protons do not interact with "dry" electrons. It appears[61] that the observed value of x_0 relates to solvated electrons. At proton concentrations below 10^{-2} M (in a 1 N solution) the $V(t)$ curve includes a slowly rising portion of 100–150 ns duration which accounts for ~ 20% of the maximum signal amplitude. In N_2O solutions ($C_a \leq 2 \times 10^{-2}$ M) a signal of this form is observed at all acceptor concentrations. This slow increase needs to be investigated further in order to establish whether it is the results of electrode or of bulk reactions of the filled acceptors, or whether it is due to the variation of x_0 with acceptor concentration.

V. TUNNELLING OF EMITTED ELECTRONS THROUGH THE POTENTIAL BARRIER AT THE INTERFACE

One of the most significant differences between photoemission into electrolyte solutions and photoemission into a vacuum is the linear dependence of the long-wave limit of the photoeffect on the electrode potential, due to the fall in potential over distances of atomic dimensions from the metal surface. It follows that tunnelling penetration of the barrier by electrons having an energy lower than the work function by an amount $e\varphi$ becomes possible.

The tunnelling model satisfactorily describes photoemission into dilute solutions and solutions containing surface-active compounds. In the former case, in addition to the potential drop across the dense part of the double layer, we have to consider the Ψ' potential, acting over distances of tens or hundreds of Ångstroms and therefore unlikely to permit tunnelling. Thus, for the case of photoemission into dilute solutions the full potential drop in Eqn. (2) should be replaced by the potential drop across the dense part of the double layer, through which the emitted electrons are able to tunnel:

$$I_0 = L(t)\chi(\hbar\omega - \hbar\omega_0 - e\varphi + e\psi')^{s/2}, \qquad (8)$$

and dilute solutions should show deviations from linearity in the $Q^{0.4}$ versus φ plots, due to the $\Psi'(\varphi)$ variation.

Eqn. (8) has been tested[18] in potassium sulphate solutions of concentration between 10^{-1} and 10^{-5} N.

In Fig. 16 the Ψ' potentials given by Eqn. (8), corresponding to the horizontal shift of the $Q^{0.4}(\varphi)$ curves in K_2SO_4 solutions with increasing dilution (with respect to the straight line for the concentrated solutions drawn so as to intersect the dilute solution curve at the point of zero

intersect the dilute solution curve at the point of zero charge), are compared with the Ψ' potentials given by the Gouy–Chapman theory for electrolyte solutions without specific adsorption. Similar results have been obtained in acid solutions[18]. Other workers[11,42] also conclude that a correction for the Ψ' potential must be applied to the photocurrent equation, but in their view the correction should be smaller than Ψ'.

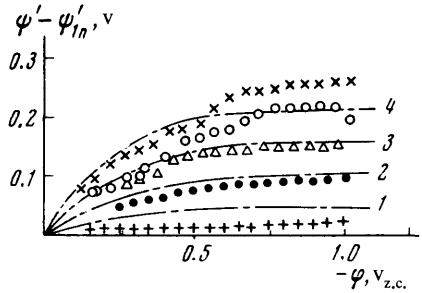

Figure 16. Shift of current–voltage curves in dilute solutions, relative to 1 N K_2SO_4 (N_2O acceptor). The broken curves correspond to the theoretical ψ' potential: *1*) 0.1 N; *2*) 0.01 N; *3*) 0.001 N; *4*) 0.0001 N.

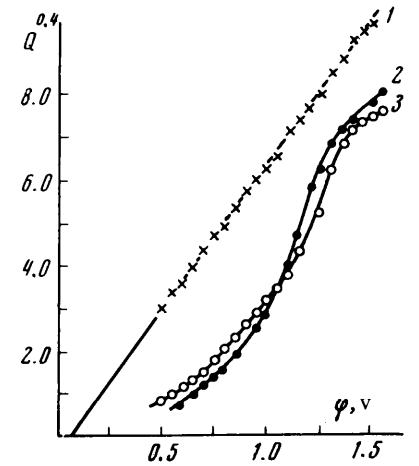

Figure 17. Current–voltage curves in solutions of caprylic and enantic acids: *1*) base solution 0.1 N KF; *2*) 0.1 N KF + 0.01 M $C_9H_{17}COOH$; *3*) 0.1 N KF + 0.01 M $C_6H_{11}COOH$.

In dilute solutions containing an acceptor, as well as in concentrated solutions, the rise time of the photopotential is the same as the duration of the light pulse, and the reverse diffusion current of solvated electrons follows any change in light intensity. In the absence of acceptors, however, the shape of the pulse changes: the initial rise is followed by a 30% fall of photopotential after approximately 5×10^{-4} s, and a more gradual decay with a time constant $RC = 0.1$ s. A signal of this form is consistent with hindered reverse flow of the solvated electrons to the electrode: a rate constant for the interaction between e_S and a water molecule agreeing with the published value[62] (2×10^3 s^{-1}) has been deduced from these data. The slope of the linear portion of the $Q^{0.4}(\varphi)$ plot increases with decreasing ionic strength of the solution, irrespective of the presence or absence of acceptors and of the kind of acceptor present, in contrast to the predictions of the theory of ionic reactions in solution[63]. This result evidently follows from the decrease in the number of electrons returning to the electrode in dilute solutions, caused by the effect of the Ψ' potential on the source function.

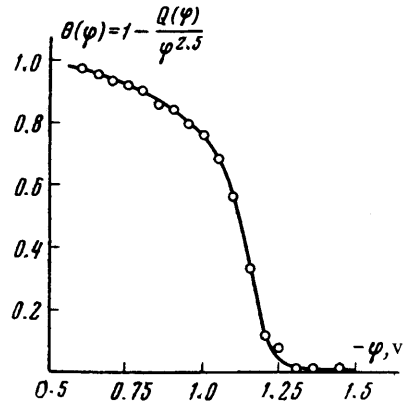

Figure 18. Coefficient $K = 1 - Q/\Delta\varphi^{5/2}$ against electrode potential in a solution of enantic acid.

The results for solutions of specifically adsorbed anions (Cl^-, Br^-, I^-) containing propanol and butanol[64,65] are in keeping with the dilution experiments. The photoemission current–voltage curve is linear when plotted as $Q^{0.4}(\varphi)$, and the work function is the same as in the solution without adsorbable ions. The tunnelling distance of the electrons is greater than the thickness of the dense part of the double layer (in NaF solution), but it is not more than 10 Å. In solutions containing surface-active compounds (s.a.c.) with molecules larger than 10 Å the $Q^{0.4}(\varphi)$ plots are S-shaped (see Fig.17)[65]. The function $\theta(\varphi) = 1 - \frac{Q}{(\hbar\omega - \hbar\omega_0 - e\varphi)2.5}$, which describes the deviation of the current–voltage curve from the "five-over-two" law, can be correlated with the coverage of the electrode surface by s.a.c. (Fig. 18), which suggests tunnelling of the electrons through surface sites not covered with adsorbed molecules. When s.a.c. are introduced into electrolyte solutions, it is necessary to allow for the effect of the adsorption Ψ' potential on the kinetics of the electrode reactions involving the species produced by the reaction between solvated electrons and acceptors (e.g. H_3O^+).[65]

VI. PHOTOEMISSION FROM METALS INTO ELECTROLYTE SOLUTIONS AS A METHOD OF STUDYING FAST REACTIONS

Photoemission from a metal into a solution has been used successfully to determine the rates of fast chemical reactions. This application of the photoemission method

is based on the separation (in time, or in terms of dependence on the electrode potential) of the primary photoemission current I_0 from the secondary currents resulting from electrode reactions of the dissolved species containing a captured emitted electron. Since photoemission itself is practically instantaneous ($\tau < 10^{-11}$ s), and the characteristic thermalisation time is even smaller, the time during which primary current flows is exactly the same as the time of illumination. The time associated with the reverse flow of solvated electrons to the electrode is of the order of $x_0^2/D_S \simeq 10^{-10}$ s, so that for illumination times $t \gg x_0^2/D_S$ the charge added to the solution by the photoemission current is

$$Q = Q_0 \frac{\left(\frac{kc}{D_s}\right)^{1/2} x_0}{1+\left(\frac{kc}{D_s}\right)^{1/2} x_0} \qquad (9)$$

It follows from Eqn. (9) that the electron-capture reaction can be investigated by measuring the function $Q(c)$. The upper limit of the illumination time ($T = 10^{-8}$ s) is set by the need to avoid complications from the relatively slow subsequent transformations of the acceptor. These slower reactions can be studied by using longer exposure times. Studies of reactions of this type, with nitrate or oxalate ions as the acceptors, have been reported[66,67].

The irreversible reactions of these acceptors involve the following scheme:

$$e_s^- + A \xrightarrow{k} A_s^-$$
$$\text{(a)}\ A_s^- \xrightarrow{\kappa_1(\varphi)} A + e_M^-$$
$$\text{(b)}\ A_s^- \xrightarrow{k_2} A_1^- + A_2$$
$$A_2 + e_M^- \xrightarrow{\kappa_2} A_2^-$$

where A is the acceptor molecule, e_S^- is the hydrated electron, A_S^- is an acceptor molecule containing a trapped electron, A_1 and A_2 are products derived from an acceptor molecule with a trapped electron, k is the rate constant of the reaction between a solvated electron and an acceptor molecule, κ_1 and κ_2 are the rate constants of the electrode reactions of A_S^- and A_2, k_2 is the rate constant for the decomposition of A_S^-. (In the range of potentials relevant to this work, κ_2 is usually large and independent of φ.)

The processes which consume A_S^- (decomposition in solution and oxidation at the electrode) are competing reactions, and can be separated by varying the electrode potential. In the potential region where κ_1 is small the electrode current is given by

$$I = I_0 - I_1 + I_{A_2}$$

When $k_2^{-1} \gg x_0^2/D$, the charge collected by the electrode due to the electrode reaction of A_2 particles is given by

$$Q_{A_2}(t) = \frac{D_{A_2} \cdot k_2}{2} \int_0^t \exp\left(-\frac{k_2 t'}{2}\right) \left\{I_0\left(\frac{k_2 t'}{2}\right) - I_1\left(\frac{k_2 t'}{2}\right)\right\} dt' \qquad (10)$$

where I_0 and I_1 are Bessel functions.

It is evident from Eqn. (10) that Q_{A_2} increases initially but tends to a constant value with a time-constant k_2. Part of the observed photocurrent ($I_0 - I_1$) follows instantaneously the intensity of the exciting light. Hence, we can distinguish the signal due to the electrode reaction of the A_2 particles from the background of the observed photocurrent, and we can evaluate k_2 (Fig. 19*a*). Thus, the lifetime of the hydrated NO_3^{2-} anion is $\tau = k_2^{-1} = 10^{-4}$ s, in good agreement with the value determined by pulse radiolysis[50].

When reactions (a) and (b) are both significant, the current–voltage characteristic of the observed photocurrent ($I = I_0 - I_1 - I_{A^-} + I_{A_2}$) is determined by the current–voltage characteristics of the individual components. For an exponential source function $f(x) = \frac{I_0}{x_0} \exp(-x/x_0)$ in the steady state,

$$I = \frac{I_0}{x_0}\left\{\frac{\lambda_1}{(\lambda_0+\lambda_1)\lambda_0} - \frac{\lambda_1^2 \varkappa_1}{[\varkappa_1 + (k_2 D_{A_2})^{1/2}](\lambda_0+\lambda_1)(\lambda_1+\lambda_2)(\lambda_0+\lambda_2)} + \right.$$
$$+ \frac{\lambda_1^2 \lambda_2}{2(\lambda_0^2-\lambda_1)^2}\left[\frac{(k_2 D_{A_2})^{1/2} - \varkappa_1}{(k_2 D_{A_2})^{1/2} + \varkappa_1} \cdot \frac{\lambda_0 - \lambda_1}{(\lambda_1+\lambda_2)(\lambda_0+\lambda_2)\lambda_2} + \right.$$
$$\left.\left. + \frac{1}{\lambda_1(\lambda_1+\lambda_2)} - \frac{1}{\lambda_0(\lambda_0+\lambda_1)} - \frac{1}{\lambda_1\lambda_2} - \frac{1}{\lambda_0\lambda_2}\right]\right\} = I_0 f(\lambda_0, \lambda_1, \lambda_2, \varkappa_1) \quad , \qquad (11)$$

where

$$\lambda_1 = \left(\frac{kc}{D_s}\right)^{1/2}; \quad \lambda_2 = \left(\frac{k_2}{D_{A_2}}\right)^{1/2}; \quad \lambda_0 = x_0^{-1} \quad .$$

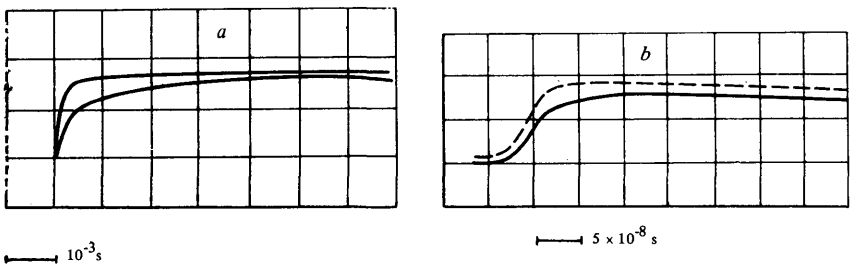

Figure 19. Photopotential in the presence of reactions in solution induced by the emitted electrons: (*a*) 1 *N* $NaNO_3$, upper and lower trace for $\varphi = -1.0$ and -1.4 V respectively; (*b*) 1 *N* $Na_2C_2O_4$, broken line is the integral of the light pulse.

Since λ_0 and λ_2 can be determined from Eqns. (9) and (10), we can evaluate the parameters of the electrode reaction of A^- by comparing the experimental function $\theta(\varphi) = Q(\varphi)(\Delta\varphi)^{-5/2}$, which gives the deviation from the "five-over-two" law, with the theoretical function $f(\lambda_0, \ldots \kappa_1)$. The function $f(\lambda_0, \lambda_1, \lambda_2, \kappa)$ is plotted against the parameter κ in Fig. 20 for $\lambda_0 = 10^6$ cm^{-1}, $\lambda_1 = 1.7 \times 10^7$ cm^{-1}, $\lambda_2 = 1.7 \times 10^4$ cm^{-1}, together with the experimental function $\theta(\varphi) = Q(\varphi)(\Delta\varphi)^{-5/2}$. The transfer coefficient $\alpha = 0.2$ and the constant

$$A = \ln k_s + \frac{\alpha e}{kT}\varphi_p = -7.6$$

can be determined by comparing the theoretical and the experimental curve.

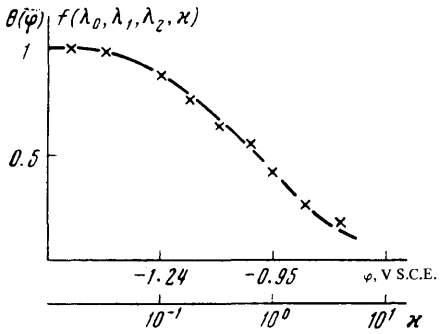

Figure 20. Comparison of the theoretical $f(\lambda_0, \lambda_1, \lambda_2, \kappa)$ (full line) and of the experimental $\theta(\varphi)$ functions.

The function $\theta(\varphi)$ in oxalate solutions is also S-shaped, with an inflection point around -1.65 V in 1 N solutions. As in the case of NO_3^- solutions, the shape of the function can be attributed to oxidation (at the electrode) of the CO_2^- ion produced from the capture of an emitted electron by an oxalate anion[27]. The resulting CO_2^- ion is oxidised at the electrode, or alternatively it can undergo chemical changes in solution when $\varphi < -1.7$ V and the rate constant of the electrode reaction is small. Since no changes in the oscillogram were noted in this region of potential, only the upper limit of the lifetime of the hydrated $C_2O_4^{3-}$ anion could be estimated ($\tau < 2 \times 10^{-6}$ s, see Fig. 19*b*).

VII. WORK FUNCTION OF ELECTRONS FROM METALS INTO POLAR SOLVENTS

The work function for the emission of electrons into water has been measured[68,69] for the following metals: Hg, Zn, Cd, Pb, Tl, Ga, Sn, Bi, Al, In, Sb, Pt, Ni, Fe, Cu, Ag, Au. With the metals whose polarisability is ideal over a sufficiently wide range, i.e. Bi, Ag, Pb, Zn, Sn, Sb, Hg, the relationship $Q^{0.4}(\varphi)$ is linear over the whole of the working range of potential, as shown in Fig. 21. The other metals have a narrower linearity region. The potential, extrapolated with respect to the reference electrode, is the same for all the metals: 0.15 ± 0.1 V S. C. E. The same conclusion was reached independently[11] for In and Tl amalgams.

The work functions of the metals, referred to published values[70] of the point of zero charge, are listed in Table 1. In most cases the difference between the water and the vacuum work function lies in the range 1.35 ± 0.15 eV.

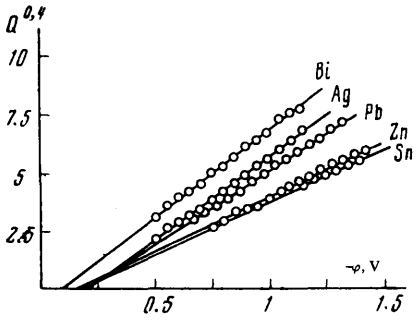

Figure 21. Emitted charge against electrode potential for various metals (0.1 N NaF + N_2O, λ = 355 nm).

The variation of the work function in water with zero-charge potential (relative to the normal hydrogen electrode) is shown in Fig. 22 for a number of metals. (The zero-charge potentials φ_0 are known with adequate precision for these metals.) The experimental dependence is described by the equation

$$\varphi_0 = \hbar\omega_0 - 3.44 \qquad (12)$$

Table 1.

Metal	Work function	Metal	Work function
Cd	2.70	Tl	2.87
Zn	2.77	In	2.90
Ag	2.77	Ga	2.90
Pb	2.91	Al	3.00
Sn	2.94	Ni	3.25
Bi	2.97	Fe	3.02
Hg	3.15	Sb	2.82
Cu	3.46	Pt	3.50
Au	3.72		

This equation allows us to convert the conventional potentials relative to the normal hydrogen electrode into the energy (relative to the free electron in a vacuum) needed to remove an electron from the metal. The constant, equal to the work function at zero hydrogen potential, can be equated to the standard hydrogen potential in electron-volts.

It should be noted that it is much simpler in practice to determine the work function from a metal into an electrolyte solution than into a vacuum, since surface states (which are known to affect the work function in vacuo) have no effect on the photoemission threshold in electrolyte solutions (see previous Section). Hence, $\hbar\omega_0$ values can be measured without special surface treatment provided that the light absorption and the electron emission take place in the metal itself.

Photoemission has been studied in polar solvents other than water in order to increase our understanding of the energetics of the process. The solvents examined include alcohols and dimethylformamide (DMF): their molecules have a capture efficiency for emitted electrons and for the products of their interaction with acceptors (H or OH') higher than the capture efficiency of water, a feature which complicates the measurement of work function.

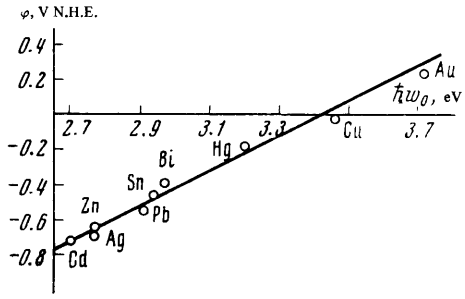

Figure 22. Work function of metals in water against potential at the point of zero charge.

Photopotential oscillograms of the normal form, and linearity of the $Q^{0.4}(\varphi)$ current–voltage characteristics, were taken as criteria for the correct choice of work function measurement conditions. With alcohols, these criteria were satisfied by using H^+ as the acceptor, and with DMF by using N_2O at sufficiently negative potentials ($\varphi < -1.1$ V S. C. E.).[69] The work functions from mercury into these solutions are given in Table 2.

Table 2. Work function of mercury in various solvents.

Solvent	$\hbar\omega_0$, eV	$W_0 - \hbar\omega_0$, eV
H_2O	3.15	1.35
CH_3OH	3.6	0.90
C_2H_5OH	3.75	0.75
DMF	3.95	0.55

The difference between the vacuum work function and the work function in the above solvents is much less than the intrinsic energy of a polaron in these media (over 3 eV). This suggests that only the electronic part of the polarisation is able to keep pace with the motion of the emitted electron at the moment when it enters the medium, and therefore $W_0 - \hbar\omega_0$ should correspond to the intrinsic energy of the electronic polaron in the medium. The slow part of the polarisation begins to relax only after the electron has been slowed down to thermal velocity ($\tau \geq 10^{-13}$ s). The calculated energies[72-74] of the electronic polaron ($E = e^2/d(1 - \varepsilon_\infty^{-1})$, where $a \simeq V_0^{1/3}$, V_0 is the volume occupied by one molecule, and ε_∞ is the optical dielectric permeability) correlate with the observed decrease of $W_0 - \hbar\omega_0$ in the sequence: water, alcohols, DMF.

Thus, the position of the conduction band in these solvents can be deduced from measurements of the work function $\hbar\omega_0$.

VIII. MULTI-PHOTON PHOTOEMISSION FROM MERCURY INTO ELECTROLYTE SOLUTIONS AND PULSE HEATING OF THE SOLUTION

When the wave-length of the exciting light is much longer than the threshold for one-electron photoemission two types of process are observed: 1) photocurrents arising from the pulse heating of the layer of solution in contact with the electrode[8] and 2) photoemission currents due to multi-photon absorption of light in the metal[9].

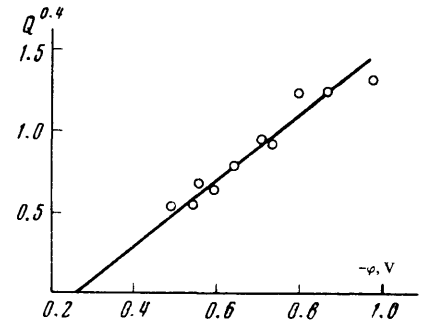

Figure 23. Emitted charge against electrode potential in 0.1 N $HClO_4$ illuminated with pulses from a ruby laser.

Table 3. Comparison of published[70] zero-charge potentials with the values obtained by the heating current method.

Metal	Potential of sign inversion	Assumed (Ref.70) values of φ_0, eV
Hg	−0.19	−0.19
Cd	−0.74	−0.72
Pb	−0.57	−0.56
Bi	−0.42	−0.40
Pt	0.10	0.11–0.19
Sn	−0.52	−0.46
Ag	−0.66	−0.70

The emission currents and the heating currents at a negatively charged mercury surface have different signs and are easily distinguished. With ruby laser light ($\hbar\omega = 1.785$ eV) the emitted charge is $Q \sim L^2$, where L is the light intensity. The current–voltage characteristic is linear in $Q^{0.4}(\varphi)$ coordinates (Fig. 23). The work function agrees with the single-photon value if the appropriate correction is made to Eqn. (2):

$$Q^{0.4} \sim 2h\omega - h\omega_0 - e\varphi. \qquad (13)$$

The characteristics observed indicate that in this case photoemission is caused by two-photon absorption in the metal. The magnitude of the emitted charge ($Q = 2.4 \times 10^{-7}$ C cm^{-2} at $\varphi = -0.5$ $V_{z.c.}$) is consistent with the theory of two-photon photoemission[75].

Upon illumination with neodymium laser light ($h\omega$ = 1.18 eV), $Q \sim L^3$, and the photoemission is associated with the absorption of three photons. The emitted charge is $Q = 8 \times 10^{-9}$ C cm^{-2} at $\varphi = -0.5$ $V_{z.c.}$.

The temperature gradient of the electrode potential on pulse heating ($10^{-3}-10^{-2}$ V deg^{-1}) is numerically equal to the temperature dependence of the double layer capacity ($\frac{1}{C}\frac{\partial Q}{\partial T} = 10^{-3}-10^{-2}$ V deg^{-1}).[76]

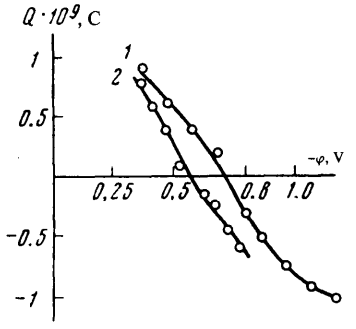

Figure 24. Integral of the heating photocurrent against electrode potential (0.1 N NaF): *1*) Cd; *2*) Pb.

The characteristics of the heating photocurrents due to the decrease in charge density of the double layer upon irradiation of the interface with pulses of long-wave light can be used to measure the point of zero charge for metals[8,77]. When $\varphi > \varphi_{z.c.}$ the heating photocurrents have a cathodic sign; on lowering the potential the photocurrent passes through zero and becomes anodic for $\varphi < \varphi_{z.c.}$ (see Fig. 24). The potentials for zero heating current, measured in this way, are consistent with the published points of zero charge for the metals[77] (Table 3).

The main advantages of this method are the ease of application to solid electrodes and the direct indication of the sign of the charge on the electrode surface.

IX. CHARGE TRANSFER THROUGH THE ELECTRODE–SOLUTION INTERFACE DURING PHOTOCHEMICAL REACTIONS IN SOLUTIONS

We have so far been concerned with the photocurrents produced by illumination of the metal–electrolyte interface. The solution was assumed to be unaffected by light, and the photocurrent was assumed to arise from emission of electrons from the metal or from ionisation of the surface donor–acceptor complexes involving the electrode as one of the components.

Photocurrents can also be produced by photochemical reactions in solution, or on the electrode surface, which are able to produce electrochemically active particles (electronically excited molecules, radicals, or stable molecules). The surface reaction is almost impossible to distinguish from ionisation of a surface complex. Photocurrents have been observed in aqueous and non-aqueous solutions of organic (aldehydes, ketones[78-80], quinones[81-83], dyes[84-86]) and inorganic compounds (metal ions of variable valency[87]). These photochemically and electrochemically active systems are highly relevant to the study of biologically important respiratory and photosynthetic processes[88,89], and also in the development of solar energy conversion devices[90,91]. Photoelectrochemistry was first widely used as a method of investigation by Berg[92], who used steady illumination in conjunction with polarography. The kinetics of formation and decay of photochemically-generated radicals were studied by solving the diffusion equation at a dropping electrode with allowance for photochemical reactions in solution and for the disappearance of radicals by various assumed mechanisms. Stable particles accumulate in the medium, and can be identified polarographically[92-95]. The mechanism of photo-reduction of quinoid compounds in aqueous solutions, and the nature of the photopotential, have been studied[92-95] by analysing the kinetic curves for the stable photolysis products constructed from polarographic data. The kinetic curve for the irreversibly formed photolysis products is S-shaped, showing that the formation reaction involves an intermediate step, and that the primary act consists in reversible photo-reduction (H_2O and OH^- being the electron donors). The photopotential varies linearly with the logarithm of the ratio of oxidised to reduced form of the compound, pointing to the reversible photolysis products[98] being the main potential-determining species in the system.

Berg[99] gave the first formulation of the problems concerning the study of excited states by electrochemical methods. The earlier workers[99-101] failed to detect photocurrents associated with electrode reactions of excited molecules because their experimental technique was inadequate: the excited states were formed too far from the electrode, and suffered deactivation before reaching the electrode by diffusion. However, Maricle and Maurer[102] were successful: they illuminated solutions of rubrene and zinc tetraphenylporphyrin in DMF through an optically transparent electrode (a film of SnO_2 deposited on glass).

For rubrene in the range of potential where the redox reaction does not give a dark current ($E_{1/2}^{Ox} = 0.95$ V, $E_{1/2}^{Red} = -1.34$ V S. C. E.), cathodic polarisation produced initially an anodic and then a cathodic photocurrent, the change of sign corresponding to a potential φ half-way between $E_{1/2}^{Ox}$ and $E_{1/2}^{Red}$. The observed photocurrent was assigned to the electrode oxidation or reduction of the rubrene singlet, whose energy is close to $E_{1/2}^{Ox} - E_{1/2}^{Red} = 2.29$ eV.[101] Illumination of zinc tetraphenylporphyrin revealed a triplet state ($E_T < E_{1/2}^{Ox} - E_{1/2}^{Red}$). Photocurrents due to the discharge of excited pyrene molecules at a semi-transparent gold electrode have also been observed[102].

Solutions of aromatic hydrocarbons in aprotic solvents are very interesting from the viewpoint of the electrochemistry of excited states, since they present the opposite problem: the electrochemical generation of excited states (electrochemiluminescence). The phenomenon has been observed during a.c. electrolysis (35–400 Hz) of rubrene, phenanthrene, pyrene, pyrylene, naphthacene, anthracene, 9,10-diphenylanthracene, 9,10-dimethylanthracene, and 3,4-benzpyrene in acetonitrile, benzonitrile, and DMF solutions with inert (usually platinum) electrodes and quaternary salts as supporting electrolytes[103-110]. Durst and Taylor[87] observed photocurrents due to excited ions at the reduction potentials of Ni^{2+} and Co^{2+}, but they did not allow for the photoemission current from the mercury electrode.

The most promising method of investigating metastable states is pulse illumination in conjunction with the relaxation methods of electrochemical kinetics[79,96]. The condition for observable photocurrent is that the lifetime of the metastable state (τ_0) should be comparable with the time of diffusion from the illuminated region to the electrode and with the time of the electrode reaction (τ_1), i.e. $\tau_0 \simeq 1/\epsilon_0^2 D$, $\tau_0 \geqslant \tau_1$, where ϵ_0 is the light absorption coefficient of the solution illuminated through the measuring electrode.

In order to observe electronically excited states ($A^* \xrightarrow{k_1} A^-$), we also require that the reverse electrode reaction of the resulting particle ($A^- \xrightarrow{k_2} A$) should be slow ($k_2 \ll k_1$).

Solution of the diffusion equation with allowance for the generation and decay of the excited states which can take part in electrode reactions gives the following expression for the total charge collected by the electrode:

$$Q = c\sqrt{\frac{D}{k_1}} \cdot \frac{\sqrt{\frac{\varkappa^2}{Dk}}}{1+\sqrt{\frac{\varkappa^2}{Dk}}} \quad , \qquad (14)$$

where c is the concentration of the particles, D is their diffusion coefficient, k is the unimolecular rate constant for the decay of excited species in solution, and κ is the rate constant of the electrode reaction.

The initial concentration of excited states is determined by the concentration of the initial compound and by the quantum yield of the photochemical reaction (usually $c \simeq 10^{-7}$ M cm^{-3}). It is found that the maximum charge collected by the electrode corresponds to $\kappa \geqslant 10^3$ cm s^{-1} for singlet excited states with $\tau_0 = 10^{-8}$ s, and to $\kappa \geqslant 10^{-1}$ cm s^{-1} for triplet states with $\tau_0 = 10^{-2}$ s. The second-order decay of the states in the bulk of the solution, e.g. by radical dimerisation or disproportionation, gives rise to a non-linear relation between the measured charge and the initial concentration of metastable states.

If the photochemical reaction in solution produces two metastable particles in a single event, the form of the electrode current will depend on the rate of the electrode reaction, the diffusion coefficient, and the direction of electron transfer through the interface for each of the particles.

We have studied[96] the photocurrents produced by illumination of aqueous solutions of riboflavin and sodium salts of the 1-, 2-, and 2,6-sulphonic acids of 9,10-anthraquinone in their absorption band, so that photoemission currents were negligible. The photocurrent pulse consists of two parts: a cathodic current with a rise time of $\leqslant 10^{-4}$ s, followed by an anodic current with a rise time of $\sim 5 \times 10^{-3}$ s. The variation of the initial part of the photocurrent with voltage, concentration, light intensity, and other parameters shows that this current is due to particles generated in the bulk of the solution, reaching the electrode by diffusion, and disappearing mainly in the bulk of the solution. The rate constant for the electrode reduction of this species is fairly large. The species could be an OH radical, formed by the reaction between an excited quinone molecule and a water molecule or a hydroxyl ion. The characteristics of the slow part of the signal indicate that the phenomenon involves oxidation and reduction at the electrode of the riboflavin semiquinones and of the anthraquinone derivatives.

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Catalytic C_6-Dehydrocyclisation of Aliphatic Hydrocarbons on Oxide Catalysts

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The results obtained during the past two decades on the dehydrocyclisation of aliphatic hydrocarbons in the presence of oxide catalysts are reviewed. New work on catalysts (composition, properties, promotion, regeneration, "development") is surveyed. Recent results are given on the dehydrocyclisation of alkanes, alkenes, dienes, and alkynes, with information on the accompanying side-reactions. A possible multistage mechanism for the dehydrocyclisation of alkanes on alumina-chrome catalysts is examined. A list of 257 references is included.

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I. INTRODUCTION

The catalytic conversion of alkanes into aromatic hydrocarbons, discovered by Soviet chemists in 1936,[1-3] allowed for the first time these two types of hydrocarbon, apparently so different in chemical properties, to be interconverted by a simple transition, without recourse to intermediate compounds containing functional groups.

This reaction was of interest to the rapidly developing petroleum industry as a potential process for the production of aromatic hydrocarbons, and came to be studied intensively in the USSR and abroad. Numerous patents appeared on procedures and catalysts for accomplishing the reaction, and from 1939 also research papers by American[4], English[5], Dutch[6], and German[7] chemists, i.e. scientists in countries having an established industry for processing petroleum or for the manufacture of liquid fuel from coal. During recent years scientists of many countries have studied this reaction, not only in connection with its practical application but also with the aim of elucidating its mechanism and kinetics. Interest has not yet died away, and during 1967–1970 new patents and papers have been published on the aromatisation of alkanes. A detailed summary of all the work up to 1947 was given in Plate's exhaustive monograph[8]. (The later reviews by Hansh[9] and by Steiner[10] were somewhat incomplete and one-sided.) The aim of the present Review is to survey work published mainly during the past twenty years.

The aromatisation of alkanes has been termed "C_6-dehydrocyclisation"[11], in contrast to the "C_5-dehydrocyclisation" of alkanes discovered by Kazanskii, Liberman, et al.[12], which occurs on platinum catalysts and yields cyclopentane and its homologues. (Henceforward we shall use the term "dehydrocyclisation" instead of "C_6-dehydrocyclisation".)

In the case of n-hexane this reaction can be represented by the overall equation

$$C_6H_{14} \rightarrow C_6H_6 + 4H_2$$

It takes place on oxide catalysts (chromic oxide without a carrier; chromic, molybdenum, tungsten, and vanadium oxides deposited on aluminium oxide) and on metallic catalysts (platinum, palladium, nickel, and other Group VIII metals on various carriers or without a carrier). The present Review covers the dehydrocyclisation of aliphatic hydrocarbons on oxide catalysts.

II. CATALYSTS FOR THE DEHYDROCYCLISATION OF HYDROCARBONS

1. Composition and Properties of the Catalysts

Almost all the catalysts for the reaction known hitherto were found during the first decade after the discovery of the dehydrocyclisation of alkanes[8]. The most active was chromic oxide deposited specially on aluminium oxide, and molybdenum oxide on alumina was rather less active. This assessment has been confirmed by recent investigations. Thus McGrath[13] compared three types of catalysts used in the petroleum-chemical industry—alumina–platinum, alumina–molybdenum, and alumina–chrome—and found the last to be the most effective for the preparation of benzene from n-hexane, while the first was the least effective; in the preparation of benzene from cyclohexane the alumina–platinum and alumina–molybdenum catalysts were similar in activity and more active than the alumina–chrome catalyst. The highest yield of benzene from methylcyclopentane was given by the alumina–platinum catalyst, and the lowest by the alumina–chrome catalyst[14]. It is not fortuitous, therefore, that most work on the dehydrocyclisation of aliphatic hydrocarbons has been done with an alumina–chrome catalyst.

Investigations during the 1950s and 1960s added little that was fundamentally new to the list of oxide catalysts for dehydrocyclisation. It was found that alkanes can undergo dehydrocyclisation on aluminium oxide containing ferric oxide[15]. Neodymium and samarium oxides also showed dehydrocyclising activity[16,17]. Minachev et al. investigated[18–22] the dehydrocyclisation of n-heptane on the oxides of neodymium, samarium, gallium, holmium, erbium, and yttrium at 530–560°C. The content of aromatic hydrocarbons in the products (at 545°C) was 9–28% depending on the oxide taken. Gadolinium oxide possessed the highest specific activity, and yttrium oxide the lowest. The activities of the rare-earth oxides were somewhat improved by depositing them on activated carbon.

Finally, oxide catalysts were used in "oxidative dehydrocyclisation" processes. Thus the dehydrocyclisation of alkanes on an alumina–chrome catalyst in the presence of sulphur dioxide has been described[23,24]. The only C_8 aromatic hydrocarbons formed by the dehydrocyclisation of n-octane on magnesium oxide in the presence of sulphur dioxide are ethylbenzene and *o*-xylene[25]: i.e. under these conditions the dehydrocyclisation of octane is not accompanied by isomerisation, as is observed in other cases.

The industrial use of alumina–chrome catalysts for the dehydrogenation of alkanes and alkenes and of alumina–molybdenum catalysts for the reforming of gasolines has promoted the study during the past 10–12 years of many properties of these catalysts, especially those based on chromic oxide. The properties of the oxides of chromium themselves have been described in some detail in the monographs of Rode[26] and Udy[27] (see also Ref. 28). Pool and McIver[29] have recently published a very interesting review of the physicochemical properties of alumina–chrome catalysts. Burwell et al.[30] published a survey (based mainly on his own work) of the chemisorption and certain catalytic properties of pure chromic oxide. Information on the oxides of molybdenum can be found in monographs by Killeffer and Linz[31] and by Perel'man and Zvorykina[32], and also in papers by Rode and Lysanova[33,34].

Several workers[35–38] studied the relation between the dehydrocyclising activity of alumina–chrome catalysts and their content of chromic oxide. Special interest attaches to comparison of dehydrocyclising activity with certain other properties of alumina–chrome catalysts. Thus Eischens and Selwood[37] studied the dehydrocyclising activity and magnetic properties of alumina–chrome catalysts containing different contents (1.5–58 wt. %) of chromic oxide. They found that the specific activity of the chromic oxide dropped sharply with increase in its content from 2.9% to 9%, after which it diminished only slightly. The magnetic properties of the specimens indicated that the chromic oxide formed individual groups of microcrystals on the surface of the aluminium oxide, and that variation in catalytic activity was associated with variation in the degree of dispersion of these microcrystals, which depended on several factors, including the concentration of chromic oxide in the catalyst.

Griffith et al.[38–41] studied the dehydrocyclising activity of pure aluminium and chromic oxides and of the mixed catalysts with different contents of the latter, as well as their adsorption properties, specific surface, electrical conductivity, and crystalline structure. In agreement with Visser[35] they found that the yield of toluene from n-heptane passes through two maxima corresponding to 30% and 70–75% of chromic oxide in the catalyst. Griffith and his coworkers established a correlation between the activation energy for the dehydrocyclisation of n-heptane and the activation energy of electrical conduction for samples having different contents of chromic oxide, and explained it on the assumption that the rate-determining stage of the overall reaction was the transfer of electrons from active centres, on which heptane is chemisorbed, to the conduction band. In their opinion the activity of the catalyst was due to the presence of a superficial highly disperse solid solution of alumina in chromic oxide, which differed from the α-phase in crystalline structure. According to Davis et al.[41] and Visser[35] the function of the alumina was to produce a developed surface on the chromic oxide (the specific surface of the catalyst increased from 45 to 306 $m^2 g^{-1}$ from pure chromic oxide to aluminium oxide[39]) and to stabilise the chromic oxide in the solid solution as a cubic phase instead of the hexagonal α-phase characteristic of pure chromic oxide.

All oxide catalysts gradually become covered with carbon deposits ("coke") during use for the high-temperature transformation of hydrocarbons. This diminishes the activity of the catalyst, which can be restored by regenerating the latter, i.e. by heating it in a current of gas containing oxygen. As a consequence of the need for the periodic regeneration of oxide catalysts for dehydrocyclisation, they are located alternately in an oxidising atmosphere (during regeneration) and in a reducing medium (during the reaction). A characteristic feature of oxide catalysts for dehydrocyclisation, which distinguishes them from aluminosilicate catalysts and pure alumina, is the periodic oxidation or reduction of metals of variable valency. For example, chromium(III) oxides are partly converted into chromium(VI) oxides and back again depending on the conditions. Study of the oxidation and reduction of the catalysts could be important for an understanding of

their catalytic activity and necessary in the practical conduct of industrial processes using alumina–chrome and alumina–molybdenum catalysts.

These aspects have been most fully studied for alumina–chrome catalysts, whose oxidation and reduction have interested many investigators[42-59]. Since detailed information on the valency states of chrome and alumina–chrome catalysts has been given in a review[29] and for pure chromic oxide in a monograph[26], we note here merely that the chromium(VI) content of the oxidised catalysts increases with rise in temperature[47] and with increase in the concentration of oxygen in the gas used for regenerating the catalyst[51]. Increase in the content of chromic oxide in the catalyst results in a decrease in the proportion which is oxidised to chromium(VI).[47] This may be due to a weakening of the effect of the carrier (alumina) and to coarser crystals of chromic oxide as its content increases[37], for according to Matsunaga[47] the coarser the microcrystals of chromic oxide the more difficult are they to oxidise.

Different oxides are formed depending on the conditions under which catalysts containing chromium(VI) are reduced. The usual product is the sesquioxide containing chemisorbed water in the form of hydroxy-groups. But the reduction of chromium trioxide deposited on silica gel at not very high temperatures yields chromium(V) oxide, to which is attributed the polymerising activity of chrome–silica gel and chrome–aluminosilicate catalysts[29,56]. Balandin et al.[49] found that the reduction of an alumina–chrome catalyst with atomic hydrogen forms chromium dioxide. Many workers consider that a small quantity of chromium(II) oxide is formed on the surface, together with chromic oxide, in the reduction of alumina–chrome and chrome–silica gel catalysts. This possibility was first pointed out by Weller and Voltz[44]. Van Reijen et al.[52] reached the same conclusion from a study of the magnetic properties and the electron spin resonance spectra of the catalysts, and Steiner[53] and Slovetskaya et al.[54,55] from the formation of hydrogen when the reduced catalyst is treated with water at high temperatures. Whether this hydrogen is evolved as a result of the reaction $2CrO + H_2O = Cr_2O_3 + H_2$ or as a consequence of the displacement by water of hydrogen adsorbed on the reduced catalyst is a matter of debate[57,60,61]. On the basis of the optical spectra of chrome–silica gel catalysts Przheval'skaya et al.[58] consider that chromium(VI) contents below 1% are reduced by hydrogen or carbon monoxide almost completely to chromium(II), a situation somewhat resembling the effect of the quantity of chromic oxide in an alumina–chrome catalyst on the extent of its oxidation.

2. Effect of the Addition of Various Oxides on the Dehydrocyclising Activity of the Catalysts

Greensfelder et al.[62] reported the promoting action of the oxides of several alkali and alkaline-earth metals on an alumina–chrome catalyst in the dehydrocyclisation of n-heptane. Kazanskii et al.[63,64] studied the effects of additions of all alkali metals and most Group II elements to an alumina–chrome catalyst on the yields of aromatic compounds in the dehydrocyclisation of n-heptane and the dehydrogenation of cyclohexane. Except in the case of lithium, the introduction of oxides of the alkali and alkaline-earth metals diminished the cracking of the hydrocarbons and had a promoting effect on the catalyst, especially noticeable in the dehydrocyclisation of n-heptane (Fig. 1). Later Timofeeva et al.[65] observed that these oxides had a similar effect in the same reactions on an alumina–chrome catalyst prepared in a different way. The promotion of an alumina–chrome catalyst by potassium oxide diminishes the formation of carbon[66] (see also Fig. 2), by increasing the activation energy of the reaction limiting carbonisation[67]. Nowak and Vieweg[68-70] have also studied the action of lithium and potassium oxides on the dehydrocyclisation of n-heptane on alumina–chrome catalysts. Nicolescu et al.[71] showed that the particular alkali-metal ion added influenced not only the activity but also the selectivity of an alumina–chrome catalyst in the dehydrocyclisation of n-octane, i.e. the relative quantities of ethylbenzene and *o*-xylene formed. The dehydrocyclising activity of alumina–chrome catalysts promoted by alkali-metal oxides was found to increase from lithium to rubidium[63,65,68]. A parallel increase occurs in the chromium(VI) content of the oxidised catalysts[68-72].

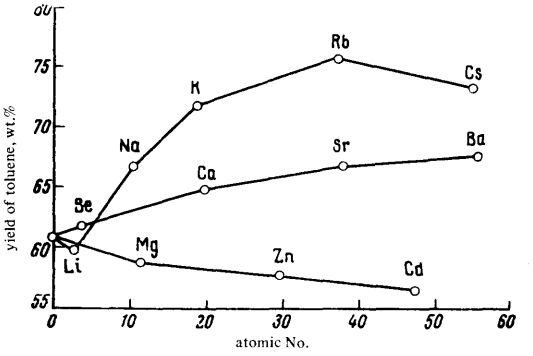


Figure 1. Yield of toluene from n-heptane on alumina–chrome catalysts to which have been added equivalent quantities of the oxides of various metals[63,64] (flow apparatus at 535°C).

It is noteworthy that the addition of potassium oxide to an alumina–chrome catalyst affects also its physicochemical properties[73-75], e.g. texture and electrical properties. Rubinshtein et al.[74] consider that addition of the potassium ion stabilises the lattice of γ-alumina.

In contrast to the promoting action of potassium oxide on an alumina–chrome catalyst, Kazanskii et al.[76] showed that it poisons pure chromic oxide for the aromatisation of n-heptane and cyclohexane at 450°C. Bridges et al.[77] later reached the same conclusion regarding the aromatisation of cyclohexane. Barium oxide has no effect on the activity of pure chromic oxide in the dehydrocyclisation of n-heptane, and somewhat increased its activity for the dehydrogenation of cyclohexane[78]. Addition of a small quantity of phosphoric acid, however, deactivated pure chromic oxide in both reactions[76].

Potassium oxide promotes also alumina–molybdenum catalysts for the dehydrocyclisation of hydrocarbons, as was shown by Bitepazh et al.[79] and independently by Rozengart and Kuznetsova[80]. Adzhieva[81] investigated the action of various quantities of magnesium oxide on an alumina–molybdenum catalyst in the dehydrocyclisation of heptane, and demonstrated a promoting effect with a small content[81]. Belen'kii and Skorupko[82] found that the yield of toluene from n-heptane on an alumina–molybdenum catalyst promoted with strontium oxide passed through a

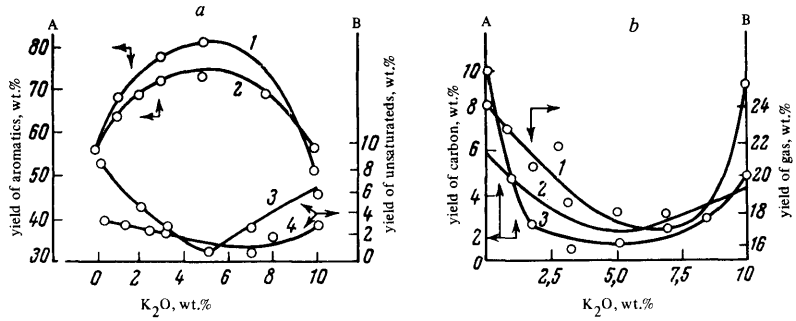


Figure 2. Effect of content of potassium oxide in alumina–chrome catalysts on yields of main products in the dehydrocyclisation of n-heptane[66] (in a flow apparatus):
(*a*): 1) aromatic hydrocarbons on catalysts of type KA-237 at 535°C; 2) aromatic hydrocarbons on catalysts of type A-30 at 550°C; 3) unsaturated hydrocarbons on KA-237; 4) unsaturated hydrocarbons on A-30.
(*b*): 1) gas on A-30; 2) carbon on KA-237; 3) carbon on A-30.

maximum (at 0.3 mole % SrO), but the yield of benzene obtained in the dehydrogenation of cyclohexane increased monotonically with increase in the strontia concentration in the catalyst.

The effect of an alkali-metal oxide depends on the quantity added to the catalyst. According to Visser[35] the maximum yield of toluene from n-heptane was obtained with the proportions $Cr_2O_3 : K_2O = 100 : 12$ with each series of catalysts containing the same total quantity of chromic oxide but different amounts of potassium oxide, independently of the proportion of the former oxide in the catalyst (over the range 40–70 mole %).

The work of Kazanskii[66], Dorogochinskii[83], and their coworkers shows that small amounts (up to 5–8 wt. %) of potassium oxide in an alumina–chrome catalyst act as a promoter, and the yield of toluene from heptane passes through a maximum as a function of this content (Fig. 2). However, comparison of the results suggests that the maximum shifts to higher contents with rise in the reaction temperature. With further increase in the content of potassium oxide (10% and above) the catalyst begins to be poisoned.

Clark[84] attributed the promoting action of alkaline additives to a diminution in the cracking and carbonising power of catalysts based on aluminium oxide. The same effect was noted by Kazanskii et al.[63], who ascribed it to a decrease in the acidity of the catalysts, and later by other workers[68] in a study of the dehydrocyclisation of hydrocarbons. Voltz et al.[85] showed that the introduction of potassium oxide into an alumina–chrome catalyst did in fact diminish its acidity. However, the role of the potassium oxide was subsequently found to be far more complicated than had been thought initially. Thus cracking and carbonisation are intensified at relatively high contents (8–10%) in the catalyst (Fig. 2*b*), which may be associated with a change in the mechanism of side reactions (see Section III, 3).[66]

It is noteworthy that the promotion of alumina–chrome catalysts produces a greater increase in the yield of toluene from heptane than in the yield of catalytic products[63,64]. Hence the promoting action of alkaline additions is not due solely to a change in the acidity of the catalyst. Starting with Voltz and Weller[45] several workers observed an increase in the content of chromium(VI) in the oxidised catalysts with increase in the quantity of potassium oxide. Results obtained by a number of workers[68,69,72,86–88,107] show that the activity of alumina–chrome catalysts increases to a limit in parallel with the increase in the chromium(VI) content in oxidised specimens, independently of whether this increase is due to the introduction of the same quantity of different alkaline additives or to different quantities of the same alkali-metal oxide. A similar parallelism between activity and chromium(VI) content is observed with samples of an alumina–chrome catalyst containing different quantities of chromic oxide[68] and with specimens which have undergone different heat-treatments[87]. All these results suggest that the activity of alumina–chrome catalysts is usually determined by the quantity of a finely dispersed microcrystalline chromic oxide phase formed on the reduction of oxygen compounds of chromium[73,107] as a carrier of active centres.

Rubinshtein et al.[73] showed that, when chromates present in an oxidised alumina–chrome–potash catalyst are reduced, the potassium ion migrates to the aluminium oxide to form surface aluminates. This was confirmed by determining the content of chromium and aluminium ions in aqueous extracts of oxidised and reduced catalysts[73,107].

Kim and Krieger[89] studied the effect of additions of silica on the dehydrocyclising activity and certain other properties of pure chromic oxide. Maximum activity for the dehydrocyclisation of n-heptane was found in a specimen containing 4.7 wt. % SiO_2. This effect was due to inhibition of the crystallisation of chromic oxide and of its dehydration during the experiments, so that deactivation of the catalyst was diminished.

3. Regeneration of Alumina–Chrome Catalysts

During the dehydrocyclisation of alkanes the activity of the catalyst varies with time (Fig. 3). If the reaction starts with an oxidised catalyst, the yield of the aromatic product increases initially, remains constant for some time, and then falls gradually, owing to the deposition of carbon on the surface of the catalyst[90]. The activity of oxide catalysts is usually restored when they are regenerated with oxygen-containing gases[91,92] or mixtures of steam and air[35,93]. No difficulties are usually involved in the regeneration of a catalyst in laboratory reaction

vessels of diameter up to 20 mm. With vessels of diameter 30 mm and larger up to industrial sizes, however, the considerable quantity of heat evolved by the combustion of carbon and the poor thermal conductivity of the layer of granulated catalyst[94] produce considerable temperature rises in the reaction vessel during regeneration of the catalyst.

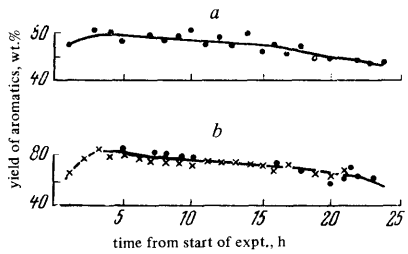


Figure 3. Variation in yield of aromatics during experiment[91] (flow apparatus, alumina–chrome catalyst, space velocity 0.35 h^{-1}) with: *a*) n-hexane at 550°C; *b*) n-heptane at 535°C.

When a stationary bed of an alumina–chrome catalyst, which has undergone carbonisation in the dehydrocyclisation of n-heptane, is regenerated with air, the carbon is burnt out layer by layer, as was established simultaneously by Modavskii and Kamusher[95] and also by ourselves[96,97]. The extent of the zone of intense combustion along the axis of the reaction vessel, the maximum temperature in this zone, and its rate of advance along the bed depend on the rate of supply of air and the distance from the start of the bed[96-98]. Oxidation of carbon in portions of the bed through which the temperature maximum has already passed takes place at a lower temperature, approximating to the temperature of the bed before regeneration began: i.e. two periods of combustion of the carbon are observed.

Comparison of the variation in the temperature of the layer of catalyst with the composition of the waste gases from the regeneration enabled Rozengart and Kazanskii to put forward in 1948 the hypothesis that the burning of carbon on an alumina–chrome catalyst occurs in the diffusion range or is subject to diffusion retardation. The presence of two periods of regeneration—the first at high temperatures and the second occurring more smoothly—is due to the different dimensions of the channels between the catalyst grains and of the pores in the grains. During the first period combustion of the carbon takes place mainly on the surface of the grains, and in the second period mainly in the pores of the catalyst.

Many workers have since arrived at similar conclusions on the presence of two periods in the regeneration of a catalyst under the influence of macrokinetic factors[86,99-101]. Rode and Balandin[102] found, in a thermographic study of alumina–chrome catalysts, including one which had become carbonised in the dehydrocyclisation of heptane, that the non-uniform composition of the carbon could also contribute to the appearance of these two periods of regeneration of the catalyst: the light components of the deposit burn out initially, and later the heavier components. The same view is held by Tyuryaev and Gusakova[103].

When regeneration is effected by a gas with a low (0.2–2%) oxygen content flowing at a high speed, the carbon burns uniformly throughout the length of the catalyst bed at a rate exceeding regeneration by air and also at a lower temperature, since part of the heat is removed by the inert gas. This method of regeneration is used in pilot plants and in industry[104]. The dynamics of combustion of the carbon is greatly influenced by its distribution and by the variation in its chemical composition along the catalyst bed. In a fluidised bed, which has good thermal conductivity and a quite uniform temperature distribution throughout the reaction vessel, carbon formed in the dehydrocyclisation of n-heptane has been shown by Novikova et al.[105] to burn uniformly throughout the bed even in a current of air in a vessel of diameter 40 mm. However, regeneration took longer in the fluidised bed than in a stationary bed.

The chemical composition of the catalyst, in particular its content of potassium oxide, has a substantial influence on regeneration[106]. The rate of combustion of the carbon was increased by the addition of 2–5% K_2O to the catalyst.

The regeneration of alumina–chrome catalysts is not confined to burning out the carbon. Restoration of their activity requires that part of the chromium(III) should be oxidised to chromium(VI).[42] This is explained by the role of oxygen compounds of chromium(VI) in producing a highly disperse chromic oxide phase, which acts as a carrier for the active centres (Section II, 2). The oxidation of chromic oxide is considerably slower than that of the carbon, and completes the regeneration of the catalyst[51].

4. "Development" and Thermal Deactivation of Catalysts

The yields of aromatic hydrocarbons obtained on regenerated oxide catalysts are extremely low initially, and gradually increase to a more or less constant level (Figs. 3 and 4).[62,90,108] This phenomenon, which has been termed "development" ("activation", "formation"[69]) of the catalyst, has considerable significance in the technology of processes using moving alumina–chrome catalysts, where they remain in the reaction zone for only 15–30 min. If a developing catalyst enters the reaction vessel, this period is so short that it functions with diminished activity, and a lower yield of aromatic hydrocarbons is obtained than on a catalyst operating with its maximum possible activity[109]. The development of alumina–chrome catalysts in the dehydrocyclisation of n-hexane and n-heptane has been studied in detail by Kazanskii, Rozengart, Dorogochinskii, and their coworkers[80,88,107-111] using a stationary bed and by Novikova et al.[112] using a fluidised bed.

When hydrocarbons are in contact with an oxidised catalyst (e.g. a regenerated catalyst) containing oxygen compounds of chromium(VI), these are reduced, while part of the hydrocarbon is oxidised to carbon monoxide, carbon dioxide, and water. This is accompanied by a rise in temperature of the layer of stationary catalyst[43,78] by 20–100 deg depending on the diameter of the reaction vessel, the initial temperature, and the chromium(VI) content of the regenerated catalyst.

Reduction of the catalyst with the formation of lower oxides of chromium is complete within a few minutes[107], but development lasts 30–40 min at 530°C. The duration of development is determined[88] by the rate of desorption of the water formed (Fig. 4), which poisons chrome catalysts for dehydrocyclisation (Ref. 8, p. 51). When the

temperature is lowered, and the rate of desorption diminishes, therefore, the development time increases, and at 470°C it is 12 h.[78] If the catalyst is first reduced with hydrogen or hydrocarbon gases, and water vapour is then desorbed by a stream of an inert gas, hardly any development of the catalyst is observed, and the latter functions with its maximum possible activity almost from the start of the reaction[88]. In industrial processes with a moving bed, therefore, the regeneration of alumina–chrome catalysts is followed by their reduction in special equipment, and only after this are they moved into the reaction vessel[113-115]. Addition to an alumina–chrome–potash catalyst of zinc oxide, boron oxide, or more aluminium oxide shortens the period of development[116]. Such rapidly developed catalysts may be of interest for processes with a fluidised bed of an alumina–chrome catalyst.

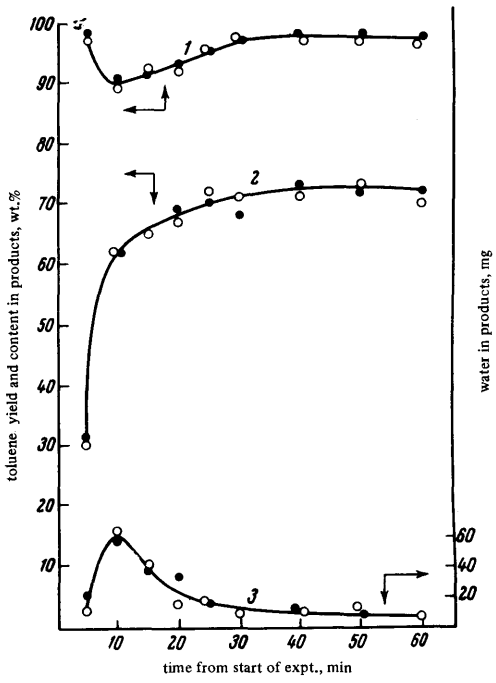


Figure 4. Variation during experiment[88] (flow apparatus at 535°C, space velocity 0.35 h^{-1}, regenerated alumina–chrome–potash catalyst) of: 1) content of aromatic hydrocarbons in products of catalysis; 2) yield of aromatic hydrocarbons; 3) content of water in products.

The development time of a stationary bed of regenerated alumina–chrome–potash catalyst in the dehydrocyclisation of alkanes corresponds to a very unusual variation in the content of aromatic hydrocarbons among the products during the experiment, represented by a characteristic "ladlelike" curve (Fig. 4, curve *1*). The left-hand, descending portion of the curve is due to increased oxidation and degradation of the less stable aliphatic hydrocarbons caused by the temperature rise at the start of the experiment. During the first 10–15 min the degradation diminishes rapidly, and the yield of catalytic products increases more rapidly than does the yield of aromatics, so that the content of the latter in the products falls. The continuing increase in the yield of aromatics, while the total yield of products remains stable, results in the content of aromatics rising to a maximum value. In a fluidised bed no rise in temperature occurs owing to its good thermal conductivity, so that the left-hand portion of curve *1* is absent[112]. The content of aromatics is lowest at the beginning of the experiment. Curves intermediate between these two extreme cases may be observed depending on the experimental conditions and the diameter of the reaction vessel, which govern the rise in temperature.

The promotion of alumina–chrome catalysts by oxides of alkali metals[107] and alkaline-earth metals[78] lowers the initial yield of aromatics and increases the development time. The principal reason is the increase in the quantity of oxygen combined with chromium(VI) on the introduction of an alkaline promoter into the catalyst, and the consequent increase in the quantity of water formed when hydrocarbons are in contact with the catalyst. Another reason is that the presence of potassium ions slows down the desorption of water[107]: i.e. it makes the surface more hydrophilic. Experiments on the dehydrocyclisation of n-heptane on an industrial alumina–molybdenum catalyst before and after promotion with potassium oxide[80] showed that development is characteristic of other dehydrocyclisation catalysts containing oxides of elements of variable valency.

According to Novikova and her coworkers[112,117] raising to 650–700°C the temperature of reduction of alumina–chrome catalysts by hydrogen or methane, or heating in a stream of helium at 700°C a catalyst which has been reduced at 530°C, halved the dehydrocyclising activity of an alumina–chrome–potash catalyst. It is noteworthy that deactivation of an alumina–chrome catalyst with rise in the reduction temperature had been observed earlier by Maslyanskii and Bursian[42] in the dehydrogenation of cyclohexane. Novikova's results[112], as well as investigations by Rozengart et al.[87], have shown that the thermal deactivation of reduced oxide–chrome catalysts is probably due to further dehydration, which facilitates recrystallisation of the microcrystals of chromic oxide. This decreases the surface associated with this oxide while having little effect, as experience shows, on the total specific surface of the catalyst. Heating in a current of air at 700°C usually restores both the activity of a catalyst deactivated in this way and apparently the surface area of chromic oxide in the catalyst which had been reduced at 530°C. In contrast to all other known cases of the thermal deactivation of catalysts, that of reduced alumina–chrome catalysts is reversible, provided that there is no change in the surface or the texture of the aluminium oxide.

III. REACTIONS INVOLVED IN THE DEHYDROCYCLISATION OF HYDROCARBONS ON OXIDE CATALYSTS

Dehydrocyclisation has been most fully studied on various alkanes; less is known about that of alkenes; and very little on the dehydrocyclisation of dienes, trienes, and alkynes.

1. Dehydrocyclisation of Alkanes

(*a*) Effect of molecular weight and structure of alkanes on composition of reaction products and yields of aromatic hydrocarbons

Oxide catalysts for dehydrocyclisation, even single-component catalysts like pure chromic oxide, and multifunctional, since dehydrocyclisation, dehydrogenation, and hydrogenation take place on them, as well as cracking, alkylation, dealkylation, and polymerisation; under certain conditions the disproportionation of unsaturated hydrocarbons can also occur. Therefore the composition of the products obtained on oxide catalysts from aliphatic hydrocarbons, in particular alkanes, is extremely complicated. The main products—the expected aromatic hydrocarbons and hydrogen—are accompanied by hydrocarbons containing either the same number of carbon atoms as the initial alkane or smaller or larger numbers. The quantitative proportions of the various groups of hydrocarbons and individual components in the products depend on the composition and the structure of the initial hydrocarbon, the reaction conditions, and the chemical nature of the catalyst.

The yields of aromatic hydrocarbon increase with the increase in molecular weight from n-hexane to n-nonane and n-decane. Values given in different papers vary within quite wide limits. The maximum yields obtained on alumina–chrome catalysts promoted with alkali metals are 65–80 wt. % based on the initial alkane.

Hexanes. Only n-hexane is able to undergo direct C_6-dehydrocyclisation: isohexanes form benzene on oxide catalysts after preliminary skeletal isomerisation [78]. The gaseous conversion products from n-hexane contain both straight-chain and branched-chain C_1–C_5 hydrocarbons (saturated and unsaturated). Rozengart et al. [78,90] found the product of catalysis (alumina–chrome–potash catalyst at 550°C) to contain, together with the initial hexane and the expected benzene, up to 3 wt. % of branched-chain hexanes, straight-chain hexenes (mainly hex-2-ene and hex-3-ene), and traces of branched-chain hexenes. The literature indicates that the catalytic conversion of hexanes yields also traces of hexadienes, cyclohexane, toluene, xylenes, ethylbenzene, and a higher aromatic. The detailed composition of the products of the dehydrocyclisation of hexanes on an alumina–chrome–potash catalyst is given by Shuikin et al. [118–121] and on an alumina–chrome catalyst by Pines and Csicsery [122]. The latter workers note that the xylenes formed by the dehydrocyclisation of hexanes usually have the equilibrium composition. The introduction of an alkaline promoter into an alumina–chrome catalyst almost completely suppresses the formation of toluene in the dehydrocyclisation of n-hexane [78]. Minachev et al. [123] obtained an appreciable quantity of toluene (up to 15% of the product at 520°C) by the dehydrocyclisation of n-hexane on an industrial alumina–molybdenum catalyst. The absence of heptanes and heptenes from the reaction products suggests that the formation of homologues of benzene in the dehydrocyclisation of n-hexane is most likely due to the alkylation of benzene by degradation products of the initial hexane.

Heptanes. Dehydrocyclisation of heptanes may be expected to yield toluene, but benzene is formed as well, and may reach up to 4 wt. % of the products obtained on an alumina–chrome–potash catalyst. Plate and Tarasova [124,125] showed that the unsaturated products of the dehydrocyclisation of n-heptane on an alumina–vanadium catalyst at 480°C comprised mainly hept-2-ene and hept-3-ene. Shuikin et al. [119] obtained a similar result. n-Heptane (on an alumina–chrome–potash catalyst) yields all n-heptenes, usually in proportions close to the thermodynamically equilibrium values, traces of branched-chain heptanes, mainly 2- and 3-methylhexanes, and also C_1–C_6 hydrocarbons with straight-chain and branched-chain structures [78].

Special attention was paid in the early work on dehydrocyclisation [8] to the effect of branching of the carbon skeleton in the alkane on the yield of aromatics. During recent years Pines and his coworkers have studied the dehydrocyclisation of isomeric heptanes (and also octanes). These investigations, which used ^{14}C-labelled hydrocarbons, gas–liquid chromatography, and sometimes also spectroscopic analysis, gave detailed information on the composition of the reaction products. Unfortunately, alumina–chrome catalysts were used, which were poisoned fairly rapidly (within 5–18 min) and in several cases also had a strong cracking effect. Therefore purely tentative conclusions concerning yields of aromatics can be obtained only from results with the initial samples during the first 5–9 min of an experiment.

Comparison of results obtained by Hoog et al. [6] with those of Pines and Dembinski [126] indicates that the yield of aromatics from n-heptane is very similar to that from 2-methylhexane and somewhat higher than the yield from 3-methylhexane. However, the latter workers themselves remark that the lower yields in the last case may be due to stronger poisoning of the catalyst.

Octanes. Study of the products of the dehydrocyclisation of octanes is of especial interest, since ring closure can occur in several ways. Thus n-octane should yield ethylbenzene and *o*-xylene.

In practice the catalytic products from n-octane contain every possible C_8 aromatic hydrocarbon, including styrene, together with benzene and toluene [127,128]. The latter are formed by the dealkylation of ethylbenzene and xylenes. Since ethylbenzene and *o*-xylene do not isomerise on oxide catalysts for dehydrocyclisation [127–131], the presence of *m*- and *p*-xylenes is explained by the isomerisation of n-octane into branched-chain octanes followed by cyclisation of the latter [128,132]. The expected aromatic hydrocarbons usually predominate on the cyclisation of any octane [127–141]. However, the catalytic products from n-octane have been found to contain also branched-chain octanes and octenes, octadienes (traces), and also lower hydrocarbons. n-Octane has been detected in the dehydrocyclisation of 3- and 4-methylheptanes [137]; n-octane, dimethylcyclohexanes, and other saturated and unsaturated cyclic hydrocarbons in the products from dimethylhexanes [135]; and small quantities of cycloalkanes, cycloalkenes, 3-ethyl-hexenes and -hexadienes, 3-methyl-hexenes and -hexadienes, and also 3-methylhexane from 3-ethylhexane [136]. On this basis Pines and his coworkers stated that the dehydrocyclisation of C_6–C_8 alkanes involves the intermediate formation of 5–8-membered cycloalkanes or their chemisorbed forms [130,131,133–137,141]. It must be noted that, by itself, the presence of any substance among the reaction products cannot prove that it is an intermediate in the main reaction: such proof requires additional evidence.

Several workers have studied the aromatisation of trimethylpentanes [142–149]. This probably requires preliminary isomerisation with lengthening of the main chain. The principal reactions of trimethylpentanes on oxide–chrome catalysts are degradation and dehydrogenation [147,148], accompanied by the formation of C_6–C_8 aromatic hydrocarbons. Among the products from 2,2,4-trimethylpentane Timofeeva et al. [145] found traces of 1,1,3-trimethylcyclopentane; but Lester, who also studied this reaction,

considers this to be a product of a secondary, not the main reaction[149].

Nonanes and higher alkanes. Relatively little work has been done on the dehydrocyclisation of nonanes and higher alkanes[118,119,140,150-157]. Several studies have been made of the dehydrocyclisation of n-alkanes of different molecular weights on alumina–chrome or alumina–molybdenum catalysts under comparable conditions: thus Shuikin et al.[118,119] studied the dehydrocyclisation of C_6-C_{10} n-alkanes, Perrée and Bloury[140] C_6-C_9, Suzumura and Yoshida[157] C_6-C_{12}, and Usov et al.[154,155] C_9-C_{16}. The bulk of the aromatic hydrocarbons are those containing the same number of carbon atoms as the initial alkane. Mono- and di-alkylbenzenes (mainly the *ortho*-isomers) are formed together with trialkylbenzenes, naphthalene, and its homologues; anthracene and phenanthrene could not be found.

The observation by the early investigators[1-3], that the composition and structure of the major portion of the aromatic hydrocarbons formed are determined by the modes of closure of a six-membered ring available to the initial alkane, can in general be regarded as confirmed. With increase in the number of carbon atoms in the initial alkane from 6 to 10 the yield of aromatic hydrocarbons becomes larger; further lengthening of the carbon chain in the alkane probably diminishes the yield.

(*b*) Influence of reaction conditions

Temperature and space velocity (contact time). There are numerous results of this type, since almost all investigators have studied more or less thoroughly the dependence of the yields of aromatic unsaturated hydrocarbons on the temperature and space velocity[8,78,117,120,125,128,152,155-164]. The general rules—increased yield of aromatic hydrocarbons with rise in the experimental temperature and increased contact time—apply to various hydrocarbons both in a stationary bed and in a fluidised bed of the catalyst.

At relatively low temperatures (300–450°C) and short contact times the main products are unsaturated hydrocarbons, chiefly alkenes[78,158,163]; under more severe conditions (500–600°C, longer periods of contact) aromatic hydrocarbons are mainly formed (50–80).[78,90,158] With rise in temperature over a wide range or increased contact time the yield of unsaturated hydrocarbons passes through a maximum (e.g. Fig. 5).[78,128,158,162] As a consequence of all the above generalisations, study of the effect of temperature or space velocity over not too wide ranges of variation in these parameters may reveal either parallel or opposite changes in the yields of aromatic and unsaturated hydrocarbons, as has been shown by Kazanskii et al.[160]

Levitskii showed convincingly[165] that the yield of alkenes and their content in the products of the dehydrocyclisation of alkanes are determined not only by the kinetics but also by the thermodynamics of the reactions. The concentration of alkenes during the dehydrocyclisation of alkanes is usually close or equal to the equilibrium value. In several cases, therefore, the decrease in the yield of alkenes beyond the maximum can be explained not only by the diminished rate of dehydrogenation of the alkane resulting from its diminished concentration but also by the displacement of the formation equilibrium of the alkene due to the rise in the concentration of hydrogen in the reaction mixture on formation of the aromatic.

Dilution and increased pressure. Plotnikov et al.[166] studied the effect of diluting n-hexane vapour with nitrogen or of a vacuum on the yield of benzene on an alumina–chrome–potash catalyst at 500°C. They found that the yield of benzene increased, while that of hexenes decreased, with decrease in the partial pressure of hexane, i.e. with increase in dilution by nitrogen or decrease in the total pressure. As these workers state correctly, the results can be explained on the assumption that benzene is formed via hexenes.

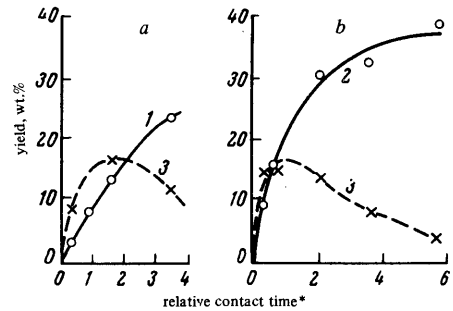


Figure 5. Effect of relative contact time* in flow apparatus[78] on yields of products from the dehydrocyclisation of: *a*) n-hexane at 550°C; *b*) n-heptane at 535°C: 1) benzene; 2) toluene; 3) unsaturated hydrocarbons.

*The relative contact time is a dimensionless quantity obtained by dividing the volume of the catalyst by the volume corresponding to the contact time adopted as unit.

Variation in the component partial pressures of the reaction mixture affects not only the total yield of aromatic hydrocarbons but also their composition. For example, Rozengart et al.[167] established that decreasing the partial pressures of all components in the dehydrocyclisation of n-octane under pulse conditions in a stream of helium produced considerable increases in the content and yield of styrene as compared with those observed in the usual flow equipment (for greater detail see Section III, 5).

Since hydrogen is a product of the dehydrocyclisation of alkanes, high pressures of the gas, as occur in the industrial process of hydroforming[14], have an especially unfavourable effect on the reaction. The influence of thermodynamic factors was examined also by Taylor and Turkevich[4] and later by Rossini et al.[168] (see also Ref. 8, p. 203) and several other authors[62,169]. It is noteworthy that the effect of the hydrogen pressure differed with alumina–chrome and alumina–molybdenum catalysts. According to Greensfelder et al.[62] the decrease in the yield of toluene from heptane with rise in the hydrogen pressure was smaller on the latter type of catalyst. This was noticed also by Maslyanskii et al.[169], who studied the hydroforming of ligroins on the two catalysts. Thus the adverse effect of hydrogen pressure on the dehydrocyclisation of alkanes is due not only to thermodynamic factors but also to the variation in the reaction velocity, which differs between the catalysts.

2. Dehydrocyclisation of Unsaturated Hydrocarbons

The catalytic dehydrocyclisation of unsaturated hydrocarbons has been studied less thoroughly than that of alkanes. However, sufficient results are known to leave no doubt that the presence of a multiple bond in a molecule facilitates its cyclisation with formation of an aromatic compound. The rate of dehydrocyclisation increases with the number of double bonds in the molecule, and hydrocarbons can be arranged in the sequence—alkanes, alkenes, dienes, trienes—with increasing rate of this reaction[170,171]. According to Kotlyarevskii et al.[172,173] alkynes are probably aromatised more rapidly than alkenes but more slowly than dienes.

(*a*) Alkenes

The structure of the aromatic hydrocarbon formed from alkenes and other unsaturated hydrocarbons is determined by that of the initial hydrocarbon, as in the dehydrocyclisation of alkanes. Therefore all that has been said concerning the composition of the aromatic products from alkanes applies also to the catalytic reactions of alkenes.

The alkene portion of the product usually comprises a mixture, in thermodynamic equilibrium, of isomers having the same carbon skeleton as the initial alkene but different positions of the double bond[78,125,140,174-177]. Arenes and alkenes in the products from alkenes are always accompanied by alkanes formed by hydrogenation of the initial hydrocarbon by hydrogen evolved in the dehydrocyclisation. Dienes[171,174,177] and traces of trienes have also been found in the products. According to Perrée and Bloury[140] the yield of aromatics rises with increase in the molecular weight of the alkene from n-hex-1- and -2-enes to the corresponding n-octenes.

Great attention has been paid to the effect of the position of the double bond in n-alkenes on the yield of aromatic hydrocarbons, since this is directly connected with the mechanism of dehydrocyclisation. According to Plate and Tarasova[124,125] the yields from hept-1-ene and hept-3-ene on an alumina–vanadium catalyst at 480°C were about the same, perhaps rather higher from the former hydrocarbon. It was observed at the same time that hept-3-ene poisoned the catalyst the more rapidly. Rozengart et al.[174] found that, on an alumina–chrome–potash catalyst at 450°C using an equimolar stream of helium in the usual flow equipment, the yield of toluene was larger from hept-2-ene than from hept-1-ene and smallest from hept-3-ene; the catalyst was poisoned most strongly by hept-3-ene, and least by hept-1-ene.

Panchenkov et al.[178,179] have recently obtained similar results to the above[174] from the dehydrocyclisation of hept-1-ene, hept-2-ene contaminated with hept-3-ene, and hept-3-ene itself on an alumina–chrome–potash catalyst in an ordinary flow apparatus. The strong effect which secondary reactions are now known to have on the main reaction, in particular the different degrees of poisoning of the catalyst in the dehydrocyclisation of individual isomers, does not always permit correct conclusions as to the reaction mechanism to be drawn from results obtained in the dehydrocyclisation of alkenes in an ordinary flow-type apparatus. This has been done by conducting the reaction under pulse conditions and analysing the reaction products by means of a capillary chromatograph.

Rozengart et al.[170,177] found that heptenes can be arranged in the sequence

cis-hept-2-ene > *cis*-hept-3-ene > *trans*-hept-3-ene > *trans*-hept-2-ene ⩾ hept-1-ene

of diminishing rate of dehydrocyclisation on an alumina–chrome–potash catalyst. Thus stereoisomerism has a greater effect than the position of the double bond on the rate of dehydrocyclisation of alkenes. The influence of branching of the carbon skeleton of alkenes on the yield of aromatics has not in fact been studied. It is interesting that 2,5-dimethylhexa-2,4-diene has been recommended as a starting material for the production of *p*-xylene[180]. Temperature and space velocity have the same effects on the yield of aromatics from alkenes as have been noted with alkanes. Cracking, the deposition of carbon, and poisoning of the catalyst are more marked in the dehydrocyclisation of alkenes[140,181].

(*b*) Dienes

Plate and Batuev[182] passed hexa-1,5-diene over an alumina–chrome catalyst at 300° and 400°C, and found 8–11% of benzene in the product. Shuikin et al.[183] studied the C_5- and C_6-dehydrocyclisation of various dienes on an alumina–chrome–potash catalyst in a vacuum, and showed that 42% of toluene is formed from hepta-1,3-diene at 600°C. When preparing *p*-xylene, Kotlyarevskii and Zanina[173] found that 2,5-dimethylhexadiene is aromatised better than is 2,5-dimethylhexene on an alumina–chrome catalyst promoted with magnesium oxide; the composition of the products from the dienes showed more individuality than those from the alkene. According to Akioshi et al.[138] the yield of aromatics obtained on a chrome–magnesia catalyst was higher from 2,5-dimethylhexa-2,4-diene than from 2,5-dimethylhexa-1,5-diene. The same yield of toluene was obtained from hepta-1,3- and -2,4-dienes on an alumina–chrome–potash catalyst at 450°C under pulse conditions[171], since the rate of migration of the double bond was higher in the dienes than in the alkenes. The heptenes (a mixture of all the n-heptenes), formed by hydrogenation of the initial diene, were accompanied in the reaction products by hepta-1,3,5-trienes, the yield of which reached 3 wt. %.[170]

(*c*) Trienes

The dehydrocyclisation of trienes on an alumina–chrome catalyst promoted with magnesium oxide has been described in a patent[184]. No other information was available on this topic before our work[170,171]. Aliphatic trienes readily undergo a peculiar thermal "cycloisomerisation" into cyclohexadienes[185-188]. According to Lewis and Steiner[188] only *cis*-hexatriene is directly cyclised, having the horseshoe configuration favourable for ring closure; other isomers first isomerise into the *cis*-form.

Rozengart et al.[170] found that hepta-1,3,5-triene is easily converted into toluene on an alumina–chrome–potash catalyst under pulse conditions in a stream of helium at 450°C. The products contained also heptadienes, formed by hydrogenation of the original triene with hydrogen resulting from the dehydrocyclisation. No cyclic hydrocarbons other than toluene and methylcyclohexadienes were detected. Komatsu has recently reported[189] that 3-methylhepta-1,4,6-triene, obtained by the dimerisation of butadiene, is converted on an alumina–chrome catalyst into a good yield of *o*- and *p*-xylenes at as low a temperature as 200°C.

(*d*) Alkynes

Information on the dehydrocyclisation of alkynes is extremely scanty. Levina et al.[190] showed that the passage of hex-1-yne and hept-1-yne over an alumina–chrome catalyst at 450°C gives yields respectively of ~25% of benzene and ~32% of toluene together with 2% of benzene.

Kotlyarevskii[191] obtained a 7% yield of aromatic hydrocarbons by passing hexadien-3-yne in a current of hydrogen over activated carbon at 500°C. On an alumina–chrome catalyst this alkenyne gave ~25% of aromatics at 450°C, and up to 85% at 500°C; in the latter experiments the products included 20% of benzene and 10% of anthracene together with naphthalene and other aromatic hydrocarbons. On the same catalyst at 400°C a yield of 24% of *p*-xylene was obtained from 2,5-dimethylhex-3-yne and up to 28% of toluene from 2-methylhexadien-3-yne.

Formation from alkynes themselves of the horseshoe configuration necessary for cyclisation may be supposed to be extremely difficult, since three or four carbon atoms lie in a straight line (in alk-1-ynes or in alk-2- and -3-ynes and hexadien-3-yne). As, however, the isomerisation of alkynes on chromic oxide yields conjugated dienes[192], it may be assumed that monocyclic aromatic hydrocarbons are formed from the dienes, not directly from the initial alkynes. Aromatic hydrocarbons having fused rings are probably formed from several molecules of the alkyne.

3. Secondary Reactions

The dehydrocyclisation of hydrocarbons on oxide catalysts is accompanied by several side reactions, which have a significant effect on the composition of the products and the yield of aromatic hydrocarbons. Amongst such reactions are cracking, the isomerisation of aliphatic hydrocarbons, the dealkylation and alkylation of aromatic hydrocarbons, carbonisation, and also the hydrogenation of unsaturated hydrocarbons. Since all these reactions other than the last are retarded when the catalysts are promoted with alkaline additions[63,66], it may be supposed that they are catalysed mainly by a carbonium mechanism involving acidic centres, and are connected with changes undergone by intermediate or initial unsaturated hydrocarbons. With a large excess of alkali-metal oxide in the alumina–chrome catalyst the mechanism of cracking and carbonisation probably changes, and these reactions begin to take place by a carbanion mechanism[66].

Cracking. This is intensified by increase in the molecular weight of the initial hydrocarbon[78,140], rise in the reaction temperature[67,140], and increase in the contact time[67,83]. Varshaver[67] has found that gas formation in the dehydrocyclisation of n-heptane on various alumina–chrome–potash catalysts is well described by a fractional linear equation.

Isomerisation. Hydrocarbons are observed to isomerise in many of their catalytic reactions, e.g. dehydrogenation of the lower alkanes[193,194]. Earlier results on the isomerisation of hydrocarbons during dehydrocyclisation were discussed in adequate detail by Obolentsev[195–197]. Isomerisation has little effect on the yield of aromatics in the dehydrocyclisation of n-hexane and n-heptane; it is responsible for the appearance of small quantities of alkanes and alkenes of branched-chain structure among the products. However, isomerisation becomes very noticeable in the dehydrocyclisation of ^{14}C-labelled heptanes and octanes. Migration of the radiocarbon atom, which has been established in these cases[122,130,141,144,198–202], is probably due to isomerisation of the carbon skeleton of intermediate unsaturated aliphatic hydrocarbons, not to peculiarities of the mechanism of dehydrocyclisation.

Hydrodealkylation. Appreciable hydrodealkylation of the aromatic hydrocarbon formed is already evident in the dehydrocyclisation of n-heptane, and leads to the formation of benzene from toluene, and to the appearance of benzene and toluene among the products of the dehydrocyclisation of octane, as stated above. On an alumina–chrome–potash catalyst the hydrodealkylation of ethylbenzene is more rapid than that of xylenes by factors of 2–10,[127] the formation of benzene from ethylbenzene probably occurring by two mechanisms—elimination of the ethyl group and initial elimination of a methyl group with subsequent detachment of a second methyl from the resulting toluene.

Alkylation. Hexane and heptane show especially appreciable alkylation of the aromatic hydrocarbons formed by dehydrocyclisation (see above discussion of the composition of the products of dehydrocyclisation). Alkylation probably occurs by a carbonium mechanism, since the introduction of potassium oxide into an alumina–chrome catalyst strongly inhibits this reaction, as has already been noted.

Carbonisation. In comparison with other side reactions carbonisation has the most adverse effect on the dehydrocyclisation of hydrocarbons, since it poisons the catalyst and makes regeneration necessary. Raising the temperature, increasing the space velocity, and extending the duration of the experimental result in increased quantities of carbon on the catalyst[67,78,203,204]. Under otherwise similar conditions the yield of carbon depends on the nature of the hydrocarbon, increasing in the sequence—cyclohexanes, alkanes, alkenes, and alkylcyclopentanes—which are converted into alkylcyclopentadienes. It follows from Section II, 2 that the yield of carbon is influenced also by the chemical composition and the properties of the catalyst, e.g. the nature of its porosity[205].

During dehydrocyclisation carbon is deposited non-uniformly along a stationary layer of catalyst[206]: the rate of deposition is highest at the beginning of the layer, and falls gradually to the end. The distribution of carbon depends also on the starting materials and the properties of the catalyst. This has been examined theoretically by Froment and Bischoff[207,208]. According to Novikova et al.[117,209] carbon is deposited uniformly throughout the mass of a fluidised bed of an alumina–chrome–potash catalyst during the dehydrocyclisation of n-heptane.

Equations for the dependence of catalyst poisoning on experiment duration in the dehydrocyclisation of alkanes have been given by Herington and Rideal[129] for an alumina–chrome catalyst, and later by Sterligov[156] for an alumina–molybdenum catalyst (see also Ref. 210 for equations describing the poisoning of a catalyst by carbon).

The carbon formed on catalysts itself catalyses the dehydrocyclisation of hydrocarbons[211], their dehydrogenation[212], and irreversible catalysis[213].

4. Kinetics of Dehydrocyclisation

Pitkethly and Steiner[5], Herington and Rideal[129], and Karzhev and Sorokin[214] assumed that the dehydrocyclisation of alkanes, in particular of n-heptane, was a first-order reaction. Griffith et al.[38] consider it to be of zero order. Tarasova and Kazanskii[158] found that dehydrocyclisation on an alumina–chrome–potash catalyst is a zero-order reaction with high rates of supply of hexane. According to Obolentsev[215] the yield of aromatic hydrocarbons and the total yield of aromatics and alkenes are exponential functions of the time of contact. Later Steiner[10] concluded that dehydrocyclisation may have a fractional order. Chinese workers[216] and later Skarchenko[217] considered that Frost's well known equation[218] gives a good description of the yield of aromatics from alkanes. According to Petrov[219] the total yield of benzene and alkenes from n-hexane can be represented by Frost's equation, but the yield of benzene requires a first-order rate equation. Panchenkov et al.[220] derived a fairly complicated kinetic equation for the dehydrocyclisation of alkanes, assuming that it involves the intermediate formation of alkenes and it accompanied by carbonisation.

Kazanskii, Rozengart, and their coworkers[206,221,222] have shown that the dehydrocyclisation of alkanes may be subject to internal diffusion retardation, which increases from hexane to heptane. The difference in the extent of diffusion retardation with different hydrocarbons depends on variations not so much in their diffusion coefficients as in their reactivities. This circumstance, and also the highly endothermic character of the reaction, leading to steep temperature gradients in the catalyst bed, together with the decrease in the activity of the catalyst during the experiments, have not always been taken into account in experiments serving as a basis for the deduction or the verification of the above kinetic equations. Therefore published kinetic parameters can be regarded only as a first approximation. Kinetic aspects of dehydrocyclisation merit special investigation in the light of modern ideas, methods, and techniques for the kinetic study of catalytic reactions[223-226].

5. Multistage Mechanism of Dehydrocyclisation

The mechanism of the dehydrocyclisation of alkanes has already been discussed for more than thirty years, but the problem has still not been finally solved. The results considered below will evidently permit a closer approach to its solution in the case of alumina–chrome–potash and alumina–molybdenum–potash catalysts, and very probably with certain other oxide catalysts.

Pitkethly and Steiner[5], Hoog[227], and later Herington and Rideal[129] assumed that the hydrocarbon molecule undergoes dissociative adsorption with formation of an alk-1-ene chemisorbed at the site of the double bond, which is converted into a chemisorbed cyclohexane and then into an aromatic hydrocarbon. Many authors have held the opinion, that an aromatic hydrocarbon is formed on chromic oxide catalysts via an alkene[219,220,228-232]. However, this has been proved for the dehydrocyclisation of alkanes only in the work of Rozengart, Kazanskii, and their coworkers with heptane on alumina–chrome–potash[174] and hexane on alumina–molybdenum–potash[233] catalysts and also with mixtures of n-hexane with labelled hex-1-ene[234].

According to the second alternative scheme of Pitkethly and Steiner[5] the alkane is present on the catalyst initially in a semi-hydrogenated state, and then forms a biradical with the chemisorbed first and sixth carbon atoms of the chain, which is subsequently converted into the aromatic hydrocarbon. The formation of alkenes is in this case a side reaction.

According to Kagan et al.[235] an alkane molecule, adsorbed on the catalyst by one carbon atom, can then be adsorbed by any other atom. If the latter is an adjacent atom, an alkene is formed; if, however, the other atom is the sixth, cyclisation occurs.

Plate and Tarasova suggested[8] that a sextet orientation of the hydrocarbon molecule is possible on an alumina–vanadium catalyst, since vanadium oxide, like chromic oxide and aluminium oxide, has the corundum type of lattice. On chemisorption on such sextets the alkane molecule forms an intermediate six-membered structure, which loses hydrogen and is converted into a benzene ring. In this case the formation of alkenes will be a side reaction, although they also are partly converted into aromatics. Plate and Tarasova do not exclude the possibility that, on a different catalyst with a distribution of active centres more favourable for the formation of alkenes, these may be the principal source of aromatic hydrocarbons. Lipovich et al.[236-238], from a study of the dehydrocyclisation on an alumina–chrome–potash catalyst of mixtures of n-heptane and n-heptenes in which one of the hydrocarbons was labelled with radiocarbon, also conclude that toluene is obtained by two routes—via alkenes desorbed into the gas phase and by a route independent of them—under the conditions of a flow experiment.

Davis[239] also supports the hypothetical sextet mechanism for the dehydrocyclisation of alkanes. He explains the fact that molybdenum oxide alone does not cause dehydrocyclisation, but is able to do so when deposited on aluminium oxide, by the absence of sextets from its crystal lattice, whereas in an alumina–molybdenum catalyst the molybdenum atoms are situated in the vacant octahedral cavities of the γ-alumina lattice, to form sextets on which the hydrocarbon molecule is chemisorbed.

Mitchell[199] explained the distribution of carbon-14 in toluene obtained from [^{14}C] heptane on the assumption that dehydrocyclisation involves the intermediate formation of a cyclopentane, which, with subsequent ring expansion or via the formation of a bicyclic hydrocarbon containing an endomethylene bridge, is converted into methylcyclohexane and then into toluene. As already mentioned, Pines and his coworkers[131,141] assume that the dehydrocyclisation of C_6-C_8 alkanes involves the formation of 5–8-membered rings, which are then converted into six-membered rings and into an aromatic hydrocarbon. However, Kazanskii, Rozengart, et al.[240-242] report that cyclohexanes or their adsorbed forms are not intermediate products on a chromic oxide catalyst, at least under pulse conditions. Hence the traces of cyclohexanes obtained in the catalytic aromatisation of alkanes are most probably products of secondary or side reactions.

Interesting information on the interaction between hydrocarbon molecule and catalyst has been obtained in a study of the adsorption and especially the chemisorption of hydrocarbons. Rubinshtein et al.[243-250] found that, contrary to the generally held view, alkanes and cyclohexane undergo chemisorption to a greater extent than alkenes or benzene on an alumina–chrome–potash catalyst, and that the chemisorption of hydrocarbons is related to their electron-accepting properties. In the opinion of Slovetskaya and Rubinshtein[250] the chemisorption of alkanes is directly connected with their subsequent dehydrogenation.

Usov et al.[252], using Balandin's method[252] to determine adsorption coefficients, also established that hexane at 490°C and heptane at 460–475°C are adsorbed on an alumina–chrome catalyst considerably better than is the corresponding aromatic hydrocarbon; at 500°C, however, the adsorption on n-heptane is almost the same as that of toluene. On an alumina–molybdenum catalyst at 480 to 490°C alkanes are adsorbed to the same extent as are aromatics.

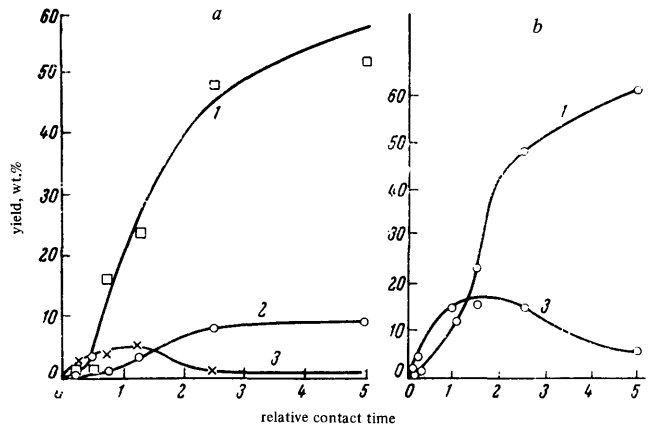


Figure 6. Dependence of yields of products of the dehydrocyclisation of hept-1-ene at 450°C on the relative contact time[172,175] (see footnote to Fig. 5) in: *a*) flow apparatus; *b*) pulse apparatus: 1) aromatic hydrocarbons; 2) n-heptane; 3) heptadienes.

A study in our laboratory of the effect of time of contact on the yield of aromatic and unsaturated hydrocarbons in the dehydrocyclisation of n-hexane, n-heptane, and n-octane on an alumina–chrome–potash catalyst in the usual flow (Fig. 5) and pulse types of apparatus has shown[78,128], in agreement with results obtained by other workers, that the yield of alkenes exceeds that of aromatics at short contact times, and passes through a maximum with increase in the contact time. The dehydrocyclisation of hept-1-ene in a stream of helium in both types of apparatus exhibits[171,174] an analogous relative arrangement of the curves for the yields of toluene and of heptadienes (Fig. 6), but in the dehydrocyclisation of hepta-1,3-diene under pulse conditions a very similar situation is observed[170,171] for the yields of aromatics and of heptatriene (Fig. 7). Indeed, it was not possible in the latter case to observe a higher yield of trienes than of toluene at short times of contact. The dehydrocyclisation of hepta-1,3,5-triene produces methylcyclohexadiene and toluene[170,171]. The yield of the latter increases with increased duration of contact with the catalyst, but the total yield of cycloalkadiene and arene remains almost constant and equal to the yield of methylcyclohexadiene in the thermal cyclisation of heptatriene under the same conditions (Fig. 8).

On the basis of the above facts Rozengart et al.[170] put forward the hypothesis that the dehydrocyclisation of alkanes is a multistage consecutive reaction:

alkane → alkenes → dienes → trienes → alkylcyclohexadienes → aromatic hydrocarbons.

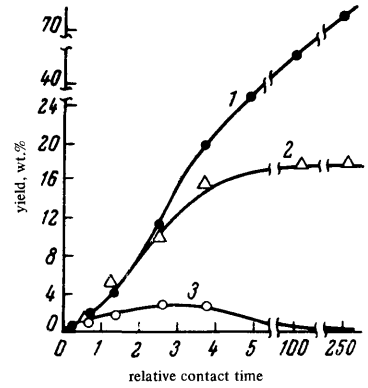


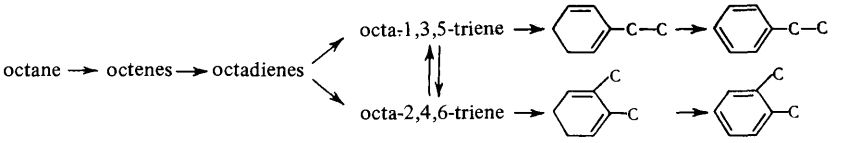
Figure 7. Dependence of product yields from the dehydrocyclisation of hepta-1,3-diene at 450°C on relative contact time (see footnote to Fig. 5) in a pulse apparatus[171,172]: 1) arenes; 2) n-heptenes; 3) heptatrienes.

All dehydrogenation stages in this scheme are catalytic, but the cyclisation stage—formation of an alkylcyclohexadiene from a triene—is thermal. Two years after publication of our results, Krause[253] suggested that heptatriene is formed in the dehydrocyclisation of heptane. In his opinion, however, toluene is formed from the intermediate heptatriene by catalytic dehydrocyclisation in a single stage, which is inconsistent with the above experimental results. The rate-determining stage of the overall process of dehydrocyclisation is probably the first stage of dehydrogenation, whatever the initial hydrocarbon—alkane, alkene, or diene.

It must be noted that our results cannot exclude the possibility of simultaneous catalytic cyclisation of part of the intermediate dienes. Since we obtained fundamentally the same results for the dehydrocyclisation of n-heptane, hept-1-ene, and n-octane in the usual flow and pulse types of equipment, the above scheme can be assumed to apply also under the conditions of the usual flow-apparatus.

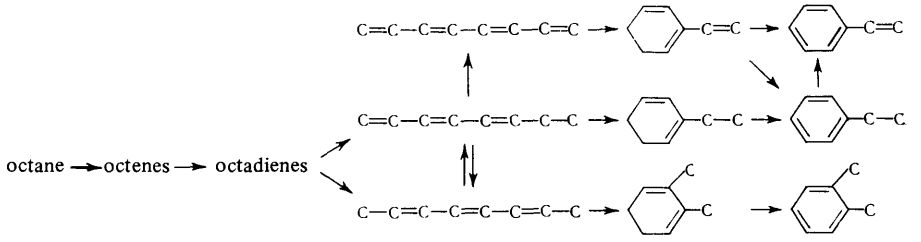
The above multistage consecutive reaction scheme has enabled us to understand certain features of the dehydrocyclisation of n-octane on an alumina–chrome–potash catalyst. Thus it has been found[167] in particular that, in experiments in pulse and flow type of apparatus, rise in temperature produces a greater increase in the yield of ethylbenzene, formed by closure of a bond between the first and sixth carbon atoms, than in that of *o*-xylene, which requires bond formation between the second and seventh carbon atoms. Variation in the relative yields of ethylbenzene and *o*-xylene cannot be a consequence of their

mutual isomerisation, because, as mentioned above, it has been established that aromatic hydrocarbons do not isomerise on chromic oxide catalysts. Since n-octane is obviously dehydrocyclised by the same scheme as has been established for heptanes, it may be supposed that in a flow apparatus ethylbenzene and *o*-xylene result from the intermediate formation of octa-1,3,5-triene and octa-2,4,6-triene respectively. The thermodynamic equilibrium of these trienes probably governs also the proportions of aromatic hydrocarbons formed in the main reaction:



From the variation in the relative yields of ethylbenzene and *o*-xylene in this series of experiments, the equilibrium shifts partly towards formation of octa-1,3,5-triene with rise in temperature.

When n-octane was diluted with helium, and especially on passing from experiments in the usual flow apparatus to pulse conditions, the yield of styrene increased[167] from 1% to 30% on an alumina–chrome–potash catalyst and to 43% on an alumina–molybdenum–potash catalyst. Analysis of the results indicated that, under pulse conditions with low partial pressures of all components of the reaction mixture (including the hydrogen formed), yields are increased in the dehydrogenation of ethylbenzene to styrene and of octa-1,3,5-triene to octa-1,3,5,7-tetraene; this last compound cyclises to vinylcyclohexadiene, which is dehydrogenated to styrene or may be partly isomerised to ethylbenzene. Therefore the scheme of conversion of hydrocarbons in the dehydrocyclisation of n-octane under pulse conditions is somewhat modified:



Under pulse conditions styrene is apparently formed in two ways, and the appearance of the second route also displaces the equilibrium between the octatrienes. As a consequence of the combined effects of dilution and rise in temperature, the products of ring closure between the first and sixth carbon atoms (with formation of ethylbenzene and styrene) come to exceed the product formed by closure between the second and seventh atoms (*o*-xylene), and the yield of styrene based on the n-octane which has reacted reaches 40% at 600°C.[167]

If the dehydrocyclisation of aliphatic hydrocarbons is assumed to comprise a series of successive dehydrogenation stages, the interaction of the hydrocarbon with the catalyst must also be considered from this point of view. The catalyst may be supposed to detach (or draw off) a proton from the hydrocarbon molecule, and the resulting carbanion is chemisorbed; or else the hydrocarbon molecule, on losing a hydrogen atom, is chemisorbed as an alkyl radical (semi-hydrogenated state). According to Myasnikov[254] such radicals, adsorbed on semiconducting oxides, are rapidly converted into a chemisorbed carbanion†. There follows detachment of a second hydrogen atom or hydride ion from an adjacent carbon atom with formation of a double bond according to the mechanism suggested by Kazanskii[255] on the basis of the atomic characteristics of chromium as a transition metal.

If the view is held that dehydrogenation begins with the detachment of one hydrogen atom, it becomes clear why dehydrogenation and then dehydrocyclisation of an alkene are more rapid than those of an alkane: detachment of a hydrogen atom or ion should occur more rapidly in the

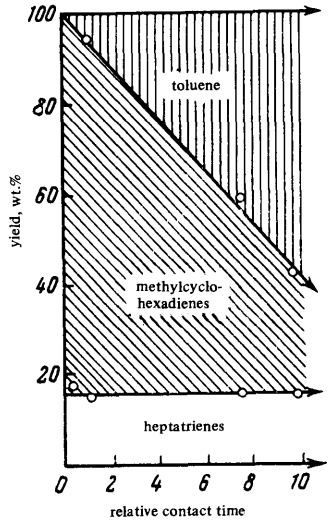


Figure 8. Dependence of product yields in the dehydrocyclisation of hepta-1,3,5-triene at 450°C in a pulse apparatus on relative contact time (see footnote to Fig. 5).[171]

† No experimental results are at present available which would allow us to assess whether the chemisorption of hydrocarbons involves rupture of a carbon–hydrogen bond or its deformation-polarisation.

allyl position, since the energy of bonding of an allylic hydrogen to carbon is smaller[256].

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The information covered in this Review indicates that the dehydrocyclisation of aliphatic hydrocarbons is quite complicated and consists of a series of successive stages. Since this reaction is accompanied by several side reactions, elucidation of the fundamental laws of dehydrocyclisation presents great difficulties; as has been shown in the Review, certain aspects of the transformation of hydrocarbons on a catalyst and the mechanism of its action are still not known accurately or may not even have been revealed. However, since new methods of investigating complicated reactions have appeared during recent years, the dehydrocyclisation of aliphatic hydrocarbons may be expected to become a favourable subject for further study, which will make an important contribution to the understanding of the fundamental principles of organic catalysis. On the other hand, the appearance of publications on industrial processes based on such reactions[43,70,180,257] provides the hope that the production of individual aromatic hydrocarbons (primarily benzene) from alkanes present in petroleum will meet with practical success.

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Lamellar Compounds of Graphite with Alkali Metals

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The preparation, structure, and thermodynamic, physical, and chemical properties of lamellar compounds of graphite with alkali metals are surveyed. These compounds are shown to be mostly similar in methods of preparation, structure, and properties to complexes of aromatic hydrocarbons with alkali metals. A list of 100 references is included.

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I. INTRODUCTION

Graphite is an allotropic modification of carbon having a layered structure. The carbon atoms are arranged in parallel planes, in each of which they form a network of hexagons in which the distance between the carbon atoms is close to the length of the carbon–carbon bond in the benzene molecule (1.415 and 1.397 Å respectively). The distance between parallel planes in graphite is rather smaller than the van der Waals thickness of aromatic molecules (3.35 and 3.4–3.5 Å), The absence of chemical bonding between the parallel carbon layers in graphite makes possible the intercalation of monatomic or monomolecular layers of various substances with formation of the so called layer or lamellar compounds of graphite. Alkali metals, halogens, strong acids, and metal halides are able to form such compounds.

Lamellar compounds of graphite with alkali metals were first obtained in 1926. They have continued to attract the attention of research workers, since they have much in common both with "solid solutions" and with the complexes formed by alkali metals with aromatic hydrocarbons. The unusual structure of lamellar compounds of graphite with alkali metals confers on them several interesting properties. Thus those with potassium, rubidium, and caesium are superconductors, react with hydrogen and nitrogen, catalyse the *ortho–para* conversion of hydrogen, and catalyse the isomerisation and the polymerisation of alkenes. We have surveyed methods for the preparation of lamellar compounds of graphite with alkali metals, their structure, and their thermodynamic, physical, and chemical properties.

II. PREPARATION OF LAMELLAR COMPOUNDS OF GRAPHITE WITH ALKALI METALS

Until recently the only method for preparing lamellar compounds of graphite with alkali metals was to heat a mixture of graphite and the alkali metal in a sealed ampoule. In this way Fredenhagen and his coworkers [1] first obtained compounds of graphite with potassium, rubidium, and caesium, having the compositions C_8M and $C_{16}M$ at 300° and 360–400°C respectively. They also investigated [2] the ability of potassium to be incorporated into graphite as a function of the pressure of its vapour. With graphite at a constant temperature (400° or 450°C) they varied the temperature of the potassium melt from 200° to 400–440°C, and obtained the compounds C_9K and $C_{18}K$. Table 1 shows that the former compound can be obtained with the graphite both at 400° and at 450°C, but this rise in temperature must be accompanied by an increase in the vapour pressure of potassium (i.e. the temperature of the melt).

Table 1. Dependence of composition of lamellar compounds with potassium on reaction conditions.

Temp. of graphite, °C	Temp. of potassium, °C	V.p. of K, mmHg	Composition of cpd.	Refs.
400	320	0.51	C_9K	2
	293	0.20	$C_{18}K$	
450	340	0.91	C_9K	2
	324	0.51	C_8K	
250–310	250	0.06	C_8K	3, 4, 5
390–425	250	0.06	$C_{24}K$	3, 4, 5
490	250	0.06	$C_{40}K$	3, 4, 5

Hérold [3–5] unlike Fredenhagen, investigated the reaction between potassium and graphite with the former at a constant temperature (250°C) while the temperature of the graphite was varied from 250° to 600°C. The isobar for the graphite–potassium system (Fig. 1) contains three plateaux at atomic K/C ratios of 0.125, 0.042, and 0.025, corresponding to the three compounds C_8K, $C_{24}K$, and $C_{40}K$. Compounds containing lower proportions of potassium could not be obtained.

Rüdorff and Schulze [6] heated a mixture of the alkali metal with graphite in a vacuum in a sealed ampoule at 300–400°C, and obtained a large number of lamellar compounds of graphite with potassium and with rubidium— C_8K, $C_{17.7}K$, $C_{21.3}K$, $C_{26.2}K$, $C_{27.7}K$, $C_{28.4}K$, $C_{29.3}K$, $C_{30.4}K$, $C_{32.7}K$, $C_{35.9}K$, $C_{38.3}K$, $C_{40.2}K$, $C_{41.3}K$, $C_{43.9}K$, $C_{44.6}K$, $C_{45.6}K$, $C_{47.9}K$, $C_{52.5}K$, $C_{56.9}K$, C_8Rb, $C_{8.6}Rb$, $C_{16.0}Rb$, $C_{24.3}Rb$, $C_{25.0}Rb$, $C_{34.8}Rb$, $C_{37.4}Rb$, $C_{50.5}Rb$, $C_{16.2}Rb$.

Ottmers and Rose [7] modified this method by using a potassium–sodium alloy, which enabled the reaction temperature to be lowered and the compounds—C_8K, $C_{24}K$, $C_{36}K$, $C_{48}K$, and $C_{60}K$—to be obtained. Penetration of sodium into graphite was not observed.

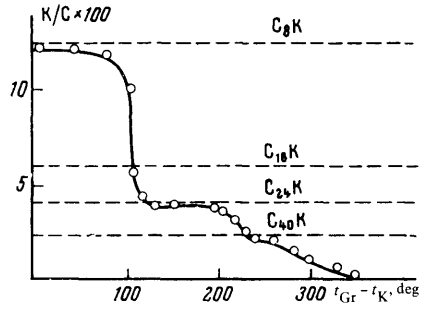

Figure 1. Dependence of composition of lamellar compounds on difference in temperature between graphite and potassium [3–5].

Salzano and Aronson [8,9] investigated the thermal decomposition of lamellar compounds of graphite with potassium, rubidium, and caesium having the composition C_8M, and discovered the existence of $C_{10}M$ between C_8M and $C_{24}M$. However, these compounds are stable only at high temperatures: $C_{10}K$ is stable at 315°C, $C_{10}Rb$ at 293°C, and $C_{10}Cs$ at 324°C.

For a long time it proved impossible [1,2,6] to obtain lamellar compounds by the direct reaction of graphite with lithium and sodium vapours. McDonnell et al. [10] and also Hennig [11] considered the formation of such compounds to be impossible, as the reduction potentials of these metals are lower than that of potassium. This view was regarded as supported by Hérold's observations [5] that a lamellar compound containing both sodium and caesium (ratio Na : Cs = 0.12) is formed by the action of an alloy on graphite, since the reduction potential of the alloy is higher than that of metallic sodium. An alloy of potassium and sodium does not produce the corresponding lamellar compound.

However, Asher and Wilson [12] showed that heating a mixture of graphite with molten sodium in an atmosphere of helium yields the same lamellar compound $C_{64-68}Na$, whose composition is independent of the temperature (120–500°C) or the duration of the reaction (from 15 min to 6 h).

Dzurus et al. [13] were unable to reproduce Asher and Wilson's results [12], and cast doubt on the existence of a lamellar sodium compound. However, Recht et al. [14] investigated the ability of graphite to absorb sodium vapour, confirmed the earlier results [12], and showed that $C_{64}Na$ is formed at 450°C after 7 days. Recht demonstrated also that the low degree of penetration of sodium is mainly kinetic in origin, since a fall in temperature leads to an increase in the equilibrium content of sodium in graphite, but considerably decreases the reaction velocity, so that below 400°C equilibrium is established with extreme difficulty.

A lamellar compound having the same composition ($C_{64}Na$) was obtained by Sleppy [15] by electrolysing molten sodium nitrate with a graphite cathode in an atmosphere of argon at 400°C. Like Hennig [13] this worker considers that the reaction is catalysed by oxygen chemisorbed on the graphite. In a study of the dependence of the diamagnetism of the compounds on the quantity of sodium incorporated Sleppy discovered a compound containing 1.95% of sodium, which corresponds to the formula $C_{96}Na$.

A small quantity of lithium was introduced into graphite [5] by electrolysing an equimolecular melt of potassium and lithium chlorides with a graphite cathode at 400°C. However, a greater amount was introduced [5] by heating lithium with graphite in a high vacuum at 500°C. Thus heating for several hours yielded a product of which the formula C_4Li was assigned. It was contaminated with lithium carbide, and increasing the duration of the reaction to 5 days resulted in complete conversion of the lithium into the carbide.

In 1965 Juza and Wehle [16] investigated the reaction between graphite and lithium vapour, and established that, depending on the conditions, lamellar compounds—C_6Li, $C_{12}Li$, and $C_{18}Li$—were formed, contaminated with lithium carbide and other lamellar graphite–lithium compounds. Bagouin et al. [17] have repeated these results, and also obtained two new compounds—$C_{36}Li$ and $C_{72}Li$.

Thus lamellar compounds of graphite with all the alkali metals can be obtained by direct reaction between the components. With potassium, rubidium, and caesium a whole set of compounds from C_8M to $C_{60}M$ have been prepared. With lithium the series begins at C_4Li and ends at $C_{72}Li$. The sodium series begins at $C_{64}Na$, probably because the conditions have not been found for preparing lamellar compounds with a high sodium content.

Table 2. Redox potentials of various aromatic hydrocarbons relative to biphenyl.

Hydrocarbon	E, V	Hydrocarbon	E, V
Biphenyl	0	Dibenz[*a*,*h*]anthracene	0.69
Naphthalene	0.09	Coronene	0.70
Phenanthrene	0.17	Perylene	1.12
Chrysene	0.38	Tetracene	1.28
Pyrene	0.60		

However, a fundamentally different method is possible for obtaining lamellar compounds of graphite with alkali metals, which utilises the aromatic character of the carbon layers in graphite. It is well known that aromatic hydrocarbons (naphthalene, anthracene, coronene, etc.) react with alkali metals in strongly ionising solvents—ammonia, amines, dimethoxyethane, hexamethylphosphoramide, etc.—to form aromatic radical-anions [18,19]. The position of equilibrium and the rate of reaction are substantially dependent on the redox potentials of the aromatic hydrocarbons under otherwise similar conditions. Paul et al. [20] and also Haijitink et al. [21] determined the redox potentials of aromatic hydrocarbons, and arranged the latter according to their electron affinity. Table 2 gives the latter workers' results [21], E being the reduction potential corresponding to formation of a monoanion.

Table 2 shows that the electron affinity increases with the number of fused aromatic rings in the hydrocarbon molecule. Therefore graphite—a compound with an infinite number of aromatic rings in a plane—should have

the highest reduction potential of all fused aromatic hydrocarbons. In such case two new methods become available for preparing lamellar compounds of graphite with alkali metals—by the reaction of graphite with solutions of (1) alkali metals and (2) aromatic radical-anions (of biphenyl, naphthalene, benzophenone, etc.).

Rüdoff et al.[22-24] showed that lamellar compounds could be prepared by the action of solutions of alkali metals on graphite. They examined the reaction of graphite with solutions of lithium, sodium, potassium, rubidium, and caesium in ammonia, methylamine, and pyridine, and found that ~2 moles of solvent per 1 g-atom of alkali metal were both incorporated into the graphite between −100° and −50°C. By using various quantities of alkali metals these workers obtained the following large number of lamellar compounds

$C_{10.6}Li(NH_3)_{1.5}$	$C_{12.5}K(NH_3)_{2.1}$	$C_{13.4}Na(NH_3)_{2.0}$
$C_{13.6}Li(NH_3)_{2.2}$	$C_{12.3}K(NH_3)_{2.3}$	$C_{16.5}Na(NH_3)_{2.2}$
$C_{15.6}Li(NH_3)_{2.0}$	$C_{23.4}K(NH_3)_{2.3}$	$C_{20.5}Na(NH_3)_{2.2}$
$C_{28.8}Li(NH_3)_{1.7}$	$C_{11.4}K(CH_3H_2)_{1.0}$	$C_{26.9}Na(NH_3)_{2.3}$
$C_{12.1}Li(CH_3NH_2)_{1.9}$	$C_{12.2}K(Py)_{1.0}$	$C_{11.9}Rb(NH_3)_{2.0}$
$C_{28}Li(H_2NCH_2CH_2NH_2)_{1.0}$	$C_{20.9}K(Py)_{0.84}$	$C_{13.8}Rb(NH_3)_{2.1}$
		$C_{12.8}Cs(NH_3)_{2.2}$

Rüdoff also found[24] that treating the potassium, rubidium, and caesium lamellar compounds with liquid ammonia resulted in the formation of ternary graphite–alkali-metal–ammonia lamellar compounds. It is interesting that part of the potassium in the compound C_8K passes into solution, and a lamellar compound $C_{12.5}K(NH_3)_2$ is formed. When, however, the compound $C_{24}K$ is treated with liquid ammonia, hardly any potassium is removed from the graphite, and the C : K ratio remains at ~28: i.e. the product has the formula $C_{28}K(NH_3)_{2.8}$. The quantity of a solvent S which is incorporated depends on its molecular size. Thus in the potassium lamellar compounds with ammonia the ratio K : S = 1 : 2; but with methylamine and with pyridine the corresponding ratio is 1 : 1.

Ginderow and Setton[25] used solutions of lithium and sodium in hexamethylphosphoramide to obtain lamellar compounds. The blue solutions of these metals react with graphite within a few seconds to form $C_{32}Li(S)$ and $C_{27}Na(S)$. Attempts to obtain lamellar compounds of potassium, calcium, magnesium, and ytterbium by this method were unsuccessful[25]. Only potassium among these four metals is slightly soluble in hexamethylphosphoramide, but the solution is unstable, and the results are difficult to reproduce. Stabilising the solution by the addition of benzene[26] results in the formation of an intense red solution, from which metal is not absorbed by graphite.

On the basis of the above principles Stein et al.[27-31] showed experimentally that lamellar alkali-metal compounds could be prepared by exchange between graphite and aromatic radical-anions. They found[31] that treating graphite with a 0.114–1.0 *N* solution of the alkali-metal–naphthalene compound in oxolan yields lamellar compounds whose composition, determined by decomposing them with acid, depends on the specimen of graphite used (Table 3).

Later investigations[27-29] indicated the following relations.

1. The equilibrium quantity of alkali metal incorporated into graphite is independent of the nature of the radical-anion (naphthalene, biphenyl, phenanthrene). However, the rate of establishment of equilibrium is sensitive to the radical-anion employed. For example, the equilibrium $ArH^{\cdot-}Li^{+}$ + graphite ⇌ ArH + graphite-Li^{+} is established more rapidly when ArH represents biphenyl than with naphthalene[28]. These results were regarded as consistent with the effect of the electrochemical potential, since the reduction potential of naphthalene relative to biphenyl is +0.9 V.

Table 3. Composition of intrusion products of alkali metals in different varieties of graphite resulting from the action of a solution of naphthalene and the alkali metal in oxolan.

Madagascar (flaky)	Ceylonese (finely ground)
$C_{41.5\pm1.5}Li$	$C_{17.5\pm1.5}Li$
$C_{120\pm4}Na$	$C_{30.5\pm1.5}Na$
$C_{81\pm2}K$	$C_{24.5\pm1}K$

2. The rate of penetration of metal into graphite varies with time during the reaction. Thus 80% of the maximum possible quantity of potassium penetrates into graphite during the first 5 h of the reaction of a potassium–naphthalene solution; the remaining 20% required 35–45 h.

3. The quantity of metal incorporated depends on the sample of graphite, far more penetrating powdered Ceylon graphite than the flaky Madagascar variety.

Table 4. Comparison of methods of analysis of products of the intrusion of an alkali metal into graphite (composition of lamellar compound from analytical data).

Metal	Ceylon graphite—analysis of		Madagascar graphite—analysis of	
	solution	compound	solution	compound
Li	$LiC_{17.6\pm1.0}$	$LiC_{17.5\pm1.5}$	$LiC_{18.8\pm1.0}$	$LiC_{43\pm3}$
Na	$NaC_{30.5\pm0.5}$	$NaC_{30.5\pm0.5}$	$NaC_{50.5\pm1.5}$	$NaC_{121\pm5}$
K		$KC_{24.5\pm1.0}$	$KC_{25.2\pm1.0}$	$KC_{32\pm2}$

4. Neither oxolan nor naphthalene is introduced with the alkali metal into the graphite. This was established by chromatography of the products of extraction at room temperature.

However, other workers have since shown conclusions 3 and 4 above to be incorrect. Thus Nominé and Bonnetain[32] have demonstrated that the different contents of alkali metal in Ceylon and Madagascar graphites are due not to differences in the structure of these specimens but to an incorrect choice of method for analysing the lamellar compounds. Since the particle size of Madagascar graphite considerably exceeds that of Ceylon graphite, the alkali metal separates completely from the latter on hydrolysis, but only partly from the Madagascar specimen. Hence the composition determined was that of the remaining solution of radical-anion, not the lamellar compound formed. Comparative data are given in Table 4.

Nominé and Bonnetain[33] also showed that the thermal decomposition products of the lamellar compounds are not binary (graphite and alkali metal) but contain also the quantities of oxolan indicated in Table 5. They found that the lamellar compound of graphite with lithium contains three phases—φ_1(Li), φ_2(Li), and φ_3(Li)—differing in the degree of solvation of lithium and in the structure of the solvate sheath of the Li^+ ion. Two phases—φ_1(Na) and φ_2(Na)—were found with sodium. It is interesting that at ~100°C the phases φ_2(Li), φ_3(Li), and φ_2(Na) pass into φ_1(Li) and φ_1(Na) with separation of part of the oxolan.

Table 5. Ratios of carbon to metal and of oxolan to metal in graphite–alkali-metal–oxolan lamellar compounds.

Metal	C/M	Ox/M
K	24±0.5	1.3±0.2
Na	32±1.5	3.5±0.3
Li	20±2.0	2.2±0.2

The graphite–potassium compound exists as a single phase. After standing at room temperature for a long time, this compound loses its oxolan completely, and passes into the binary compound $C_{24}K$. Rose et al.[34] confirmed the presence of oxolan in the compound. They also showed that lamellar compounds of graphite with alkali metals contain also small quantities of naphthalene, 1,2-dihydronaphthalene, and tetrahydronaphthalene.

Table 6. Content of oxolan (molar ratio Ox/M) in compounds formed by different varieties of graphite with alkali metals.

M	Ceylor	Madagascar
Li	0.115	0.122
Na	0.133	0.04
K	0.09	0.5

Thermogravimetric examination[34] of the specimens in a vacuum showed that only part of the oxolan is lost at 20°C and 0.001 mmHg (Table 6). With gradual rise in temperature two inflections appear on the thermogravimetric curve, which supports Bonnetain's suggestion[33] that several phases, differing in degree of solvation, exist in a single compound.

Ketyls, as well as aromatic radical-anions, are able to function as carriers of the alkali metal to the graphite. Genderow and Setton[35] established that sodium and potassium benzophenone ketyls react with graphite (particle size < 50 μm) in oxolan (Ox) solution to form the ternary lamellar compounds $C_{64}Na.Ox$ and $C_{72}K.Ox$ respectively.

Thus the reactions of graphite with solutions of alkali metals and with radical-anions show an analogy between the properties of graphite and those of aromatic hydrocarbons: (1) like aromatic hydrocarbons[36] graphite forms complexes with alkali metals (mainly with potassium) in the absence of a solvent; (2) in the presence of solvents graphite, like aromatic hydrocarbons[37], forms complexes with lithium and sodium; and (3) since the redox potential of graphite would be higher than those of aromatic hydrocarbons, graphite undergoes exchange reactions with the latter

$$ArH\div M^+ + Ar'H \rightleftarrows ArH + Ar'H\div M^+$$

to form lamellar compounds.

III. THERMODYNAMIC PROPERTIES OF LAMELLAR COMPOUNDS OF GRAPHITE WITH ALKALI METALS

Many studies have been made of the thermodynamic properties of the alkali-metal compounds of graphite[2,5,8–10,38–52].

Table 7 gives the calorimetrically determined heats of formation of lamellar compounds C_8M with potassium, rubidium, and caesium and of $C_{24}K$ from graphite and the molten metal. The stability of the C_8M compounds is seen to increase from potassium to rubidium. The heat of reaction is substantially dependent on the type of graphite, the value for the artificial material exceeding by 10 kcal g^{-1} that for natural graphite in the reaction with potassium.

Table 7. Heats of reaction of graphite with alkali metals in the range 66–95°C.

Reaction (solid)	(liq.)	(solid)	kcal g-atom^{-1} M	Ref.
8C	+K	$\rightarrow C_8K$	7.8	38
			8.35	39
			8.35	48
			6.60	52
8C	+Rb	$\rightarrow C_8Rb$	11.1	39
			11.1	48
8C	+Cs	$\rightarrow C_8Cs$	15.3	39
			15.3	48
24C	+K	$\rightarrow C_{24}K$	11.9	52

From the vapour pressure of the metal over the potassium, rubidium, and caesium lamellar compounds Hérold[5] determined the heats of formation of C_8M from $C_{24}M$ [$C_{24}K + 2K(liq.) \rightarrow 3_8K + 2Q$] in the temperature range 417–669°C as respectively 3.4, 5.85, and 10.1 kcal g-atom^{-1} M, where M = K, Rb, Cs. Later, however, Salzano and Aronson[9,40–42] cast doubt on the reliability of these values, since Hérold had been unaware of the existence of the compound $C_{10}M$ between C_8M and $C_{24}M$. Setton[45,50] calculated the work required to separate the carbon networks of graphite and the energy of bonding of 1 g-atom of potassium with carbon as respectively H_C = 2.25 kcal g-atom^{-1} C and H_K = −10.4 kcal g-atom^{-1} K at 420°K; the corresponding values calculated for 620°K were 1.73 and −6.85. The work necessary to separate the carbon networks to infinity has also been determined by several authors, and lies in the range 0.9–1.5 kcal g-atom^{-1} C.[42,53–56] From these data Setton calculated

the heats of formation of C_8K and $C_{24}K$ as respectively 6.87 and 13.3 kcal g-atom^{-1} K, which agreed with the results in Ref. 52 (see Table 7).

The thermodynamic properties of graphite–alkali-metal systems have been investigated in greatest detail by Salzano and Aronson[9,40-44]. They examined the variation in the rate of decomposition of the lamellar compounds C_8M (M = K, Rb, Cs) over the range 400–750°C, and showed that the curve contains a series of breaks corresponding to formation of the compounds $C_{10}M$, $C_{24}M$, $C_{36}M$, $C_{48}M$, and $C_{60}M$. The portions between the breaks were linear, and corresponded to the two-phase regions

(solid) (gas) (solid)

$$4\,C_{10}M + M \rightleftarrows 5\,C_8M$$
$$^5/_7\,C_{24}M + M \rightleftarrows {}^{12}/_7\,C_{10}M$$
$$2\,C_{36}M + M \rightleftarrows 3\,C_{24}M$$
$$3\,C_{48}M + M \rightleftarrows 4\,C_{36}M$$
$$4\,C_{60}M + M \rightleftarrows 5\,C_{48}M$$
$$5\,C_{72}M + M \rightleftarrows 6\,C_{60}M$$

Table 8. Thermodynamic properties of potassium, rubidium, and caesium compounds of graphite ($-\Delta H^\circ$ in kcal g-atom^{-1} M; $-\Delta S^\circ$ in cal deg^{-1} g-atom^{-1} M).

Stage	Equilibrium reaction (solid) (gas) (solid)	Graphite-K		Graphite-Rb		Graphite-Cs	
		$-\Delta H^\circ$	$-\Delta S^\circ$	$-\Delta H^\circ$	$-\Delta S^\circ$	$-\Delta H^\circ$	$-\Delta S^\circ$
Ia	$C_{24}M + M \rightleftarrows C_8M$	27.4	25.7	—	—	—	—
Ib	$4C_{10}M + M \rightleftarrows 5C_8M$	38.0	44	33.9	42.2	43.8	43.4
II	$5/7C_{24}M + M \rightleftarrows 12/7C_{10}M$	24.0	24	25.3	19.2	29.6	19.6
III	$2C_{36}M + M \rightleftarrows 3C_{24}M$	27.7	20.6	27.2	17.0	32.7	18.7
IV	$3C_{48}M + M \rightleftarrows 4C_{36}M$	30.0	20.7	29.5	17.6	34.2	18.6
V	$4C_{60}M + M \rightleftarrows 5C_{48}M$	30.6	20.8	31.0	12.3	34.9	18.6
VI	$5C_{72}M + M \rightleftarrows 6C_{60}M$	—	—	31.8	18.1	35.8	18.8

Salzano and Aronson found that the decomposition curves for lamellar compounds of composition intermediate between C_8M and $C_{24}M$ or between $C_{24}M$ and $C_{36}M$ coincide with those for C_8M: i.e. breaks are observed on the curves at the same compositions, and the rates of decomposition of the intermediate compounds are equal to those of C_8M. This was regarded as indicating that the composition and the structure of any compound are independent of its method of preparation. Thus the decomposition of lamellar compounds with alkali metals is an equilibrium process, since the constancy of the rate of decomposition with time in each two-phase region can be explained by equilibrium between the phase undergoing decomposition and that which is formed. However, the form of the decomposition curve remained unchanged for lamellar compounds with alkali metals and in a vacuum (i.e. in the absence of the metal vapour). From this it was concluded that the rate of decomposition was determined by the rate of removal of metal adsorbed on the surface of the specimen:

$$\text{M (in sample)} \overset{\text{rapid}}{\rightleftharpoons} \text{M (on surface)} \overset{\text{slow}}{\rightleftharpoons} \text{M (in vapour)}$$

This enabled ΔH° and ΔS° to be calculated for the different stages of decomposition (Table 8). The heat and the entropy of formation of the alkali-metal compounds of graphite from the elements (ΔHform and ΔSform) are given in Table 9.

The heats of formation of C_8M (M = K, Rb, Cs) found by these workers agree with calorimetric values[9] when it is remembered that the heats of evaporation of these three alkali metals (in kcal g-atom^{-1} M) are respectively 20.2 (at 550°), 17.8 (800°), and 16.8 (800°C) (cf. Tables 7 and 9). Comparison of the enthalpy and the entropy of reaction between the gaseous metal and the alkali-metal–graphite compounds (Table 8) for potassium, rubidium, and caesium shows that compounds at the same stages are formed in all three systems.

Table 9. Entropy and heat of formation of alkali-metal compounds of graphite from the elements ($-\Delta H$form in kcal g-atom^{-1} M; $-\Delta S$form in cal deg^{-1} g-atom^{-1} M).

Reaction (solid) (gas) (solid)	Graphite-K		Graphite-Rb		Graphite-Cs	
	$-\Delta H_{form}$	$-\Delta S_{form}$	$-\Delta H_{form}$	$-\Delta S_{form}$	$-\Delta H_{form}$	$-\Delta S_{form}$
$8C + M \rightarrow C_8M$	28.5	24.0	28.8	23.3	34.2	24.0
$10\,C + M \rightarrow C_{10}M$	27.0	22.5	27.5	18.5	32.2	19.2
$24C + M \rightarrow C_{24}M$	30.4	20.7	30.6	17.6	34.8	18.7
$36C + M \rightarrow C_{36}M$	31.7	20.7	32.2	18.0	35.8	18.7
$48C + M \rightarrow C_{48}M$	32.3	20.7	33.1	18.1	36.4	12.8
$60C + M \rightarrow C_{60}M$	32.8	20.8	33.6	18.1	36.7	18.8

The heat of reaction is largest for stage (Ib), is least for stage (II), and increases slightly on passing from stage (III) to stage (VI). The entropy of reaction is approximately the same for the lower stages, and has the approximate values 20.7, 17.8, and 18.7 kcal deg^{-1} g-atom^{-1} M for the potassium, rubidium, and caesium lamellar compounds. Nevertheless, the entropy is very high (42–44 kcal deg^{-1} g-atom^{-1} M) for stage (Ib) (Table 8). The large entropy changes for this stage are regarded by the authors as attributable both to the increase in concentration of alkali-metal ions in a layer and to a strengthening of interaction between adjacent layers of alkali-metal atoms.

IV. STRUCTURE OF LAMELLAR COMPOUNDS OF GRAPHITE WITH ALKALI METALS

The X-ray method usually employed for studying lamellar compounds with alkali metals enables us to determine the stage reached in compound formation, i.e. to determine the number of carbon networks of graphite associated with one layer of the metal (Fig. 2), to calculate the identity period I_c along the c-axis, to determine the thickness I_c' of a filled layer, to determine the structure of a layer of alkali metal in the graphite, and also to ascertain whether the carbon layers undergo mutual displacement on the intrusion of alkali metal.

1. Structure of Binary Systems formed by Graphite with Potassium, Rubidium, and Caesium

Several investigations have been made on the structure of lamellar compounds of graphite[5-7,57-59]. Schleede and Wellmann[59] showed that the structure of the compounds C_8M (M = K, Rb, Cs) corresponds to stage (I): i.e. a

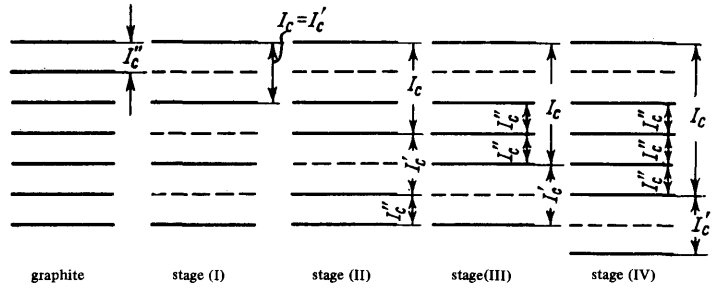

Figure 2. Arrangement of layers of graphite and of alkali metals in lamellar compounds: full line = carbon layer; broken line = intercalated metal layer; I_c'' = thickness of unfilled layer in lamellar compound; I_c = identity period in inclusion compounds; I_c' = thickness of filled layer in lamellar compound.

metal layer alternates with a graphite layer. The composition $C_{16}M$ represents the second stage of lamellar compounds. In both cases the metal atoms form a monatomic layer midway between adjacent carbon layers of the graphite. In an actual layer the metal atoms form a triangular network, the distance between them being 4.90 Å (Fig. 3). It was assumed that the carbon networks underwent no relative displacement on penetration of the alkali metal, and the identity period I_c for these compounds was determined from reflections of the type $00l$ (Table 10). If the thickness of a filled layer (Fig. 3) is assumed to be the same in compounds of both stages (I) and (II), the interplanar distance in an unfilled graphite layer is the same as in the original graphite (Table 10).

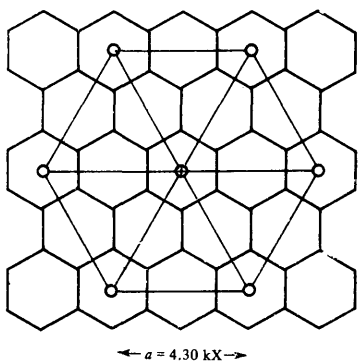

Figure 3. Triangular arrangement of potassium atoms relative to carbon network of graphite.

Subsequently Hérold [5] and especially Rüdorff and Schulze [6] made a more detailed investigation of the structure of the potassium and rubidium lamellar compounds, with the results indicated below.

1. The composition $C_{16}M$ represents a mixture of compounds of stages (I) and (II) (Table 11), the latter compound having the formula $C_{24}M$. Thus the lamellar compounds have the following compositions depending on the stages—C_8M (stage I), $C_{24}M$ (II), $C_{36}M$ (III), $C_{48}M$ (IV), and $C_{60}M$ (V).

Table 10. Identity period I_c, thickness of filled layers I_c', and thickness of unfilled layers I_c'' in lamellar compounds of graphite with potassium, rubidium, and caesium.

Metal	Colour	Stage	I_c, Å	I_c', Å	I_c'', Å
K	brown	I	5.33	5.33	3.41
	black	II	8.74	5.33	
Rb	brown	I	5.68	5.68	3.29
	black	II	8.97	5.68	
Cs	brown	I	5.94	5.94	3.31
	black	II	9.25	5.94	

Table 11. Composition and stages of compounds of graphite with potassium and rubidium.

Potassium compounds				Rubidium compounds	
composition	stage	composition	stage	composition	stage
C_8K	I	$C_{38,3}K$	III	$C_{8.2}$ Rb	I
$C_{17.7}K$	II+I	$C_{40,2}K$	III+IV	$C_{8,8}$ Rb	I
$C_{21.3}K$	II	$C_{41.3}K$	III+IV	$C_{16.0}Rb$	I+II
$C_{26.2}K$	II	$C_{43,9}K$	IV+III	$C_{24.3}Rb$	II
$C_{27.7}K$	II	$C_{44,6}K$	IV+III	$C_{26.6}Rb$	II
$C_{28.9}K$	II+III	$C_{45.6}K$	IV	$C_{34.8}Rb$	III
$C_{29.3}K$	II+III	$C_{47,9}K$	IV	$C_{37.4}Rb$	III
$C_{30.4}K$	II+III	$C_{52,5}K$	V+IV	$C_{50.5}Rb$	IV
$C_{32.7}K$	III+II	$C_{56.9}K$	V	$C_{61.2}Rb$	V
$C_{35.9}K$	III				

2. Determination of the identity periods for the lamellar compounds of stages (I)–(V) (Table 12) indicated that the thickness of a filled graphite layer is the same for all stages with a given metal, and depends only on the nature of the metal. These workers also confirmed that interplanar distances in an unfilled graphite layer were the same as in graphite itself (Table 12).

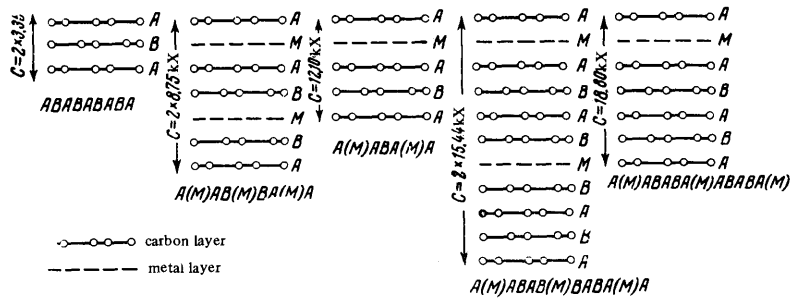

Figure 4. Relative positions of carbon networks and layers of alkali metal in lamellar compounds of graphite.

3. On passing from (I) to higher stages not only does the number of carbon networks per metal layer increase, but also the structure of the metal layer changes. Whereas the metal atoms in the compound C_8M are arranged in a triangular pattern (Fig. 3), on passing to stage (II) they are rearranged into a hexagonal network.

Table 12. Repeat periods of lamellar compounds of graphite with potassium found from 00*l* reflections.

Stage	Potassium cpd.	Rubidium cpd.
I	5.40=5.40	5.65=5.65
II	8.75=5.40+3.35	9.02=5.67+3.35
III	12.10=5.40+2·3.35	12.34=5.64+2·3.35
IV	15.46=5.41+3·3.35	15.75+5.70+3·3.35
V	18.80=5.40+4·3.35	19.08=5.68+4·3.35

This requires that the central atom (denoted by a "plus" in Fig. 3) should move out of the lattice. This could not be demonstrated by means of X-rays, since the lines *h*0*l* and *hkl* were absent from the Debye diagrams. Their absence was attributed to the great mobility of the metal atoms in the graphite planes.

4. On the formation of lamellar compounds with alkali metals the carbon networks adjacent to a metal layer shift and become superimposed (AA... BB). The remaining carbon networks are arranged as in graphite (ABAB...) (Fig. 4).

5. The identity period for the first stage should be quadrupled in comparison with that found from 00*l* reflections, since the 10*l* and 11*l* reflections have established that the alkali-metal layers are displaced relative to one another by $\frac{1}{2}0$, $\frac{1}{2}\frac{1}{2}$, and $0\frac{1}{2}$. For stages (II) and (IV) the identity period I_C calculated from 00*l* reflections should be doubled, as is indicated by the value of I_C calculated from 10*l* reflections. For stages (III) and (V) the same value of I_C is obtained by calculation from 00*l* and from 10*l* reflections.

6. Metal atoms are located below the centres of the carbon hexagons in the graphite network, and the distance between the metal atom and a carbon atom is 3.05 and 3.16 Å in the compounds C_8K and C_8Rb respectively.

More recent investigations by Nixon and Parry[57] have shown that the carbon networks adjacent to a potassium layer undergo a complete displacement: i.e. these carbon networks are equivalent. However, carbon networks remote from the potassium layer are only partly displaced. Thus some turbostrasis is observed in the arrangement of the carbon networks in lamellar compounds of graphite with potassium of stages (I)–(IV). These workers therefore suggest the arrangement

II stage — AB (K) BC (K) CA (K) A
III stage — ABA (K) ACA (K) A
IV stage — ABAB (K) BCBC (K) CACA (K) A

for the carbon networks in the potassium compounds of stages (II)–(IV).

The identity period I_C calculated by these workers for the potassium compound of stage (II) would cover three filled layers (each 5.4 Å) and three unfilled layers (each 3.3 Å), and should be 26.25 Å. In stage (III) it would contain two filled and four unfilled layers and be 24.2 Å in stage (IV) three filled and nine unfilled layers would make the identity period 46.35 Å. Good agreement was found between experimental and calculated values of the identity period.

2. Structure of Binary Compounds of Graphite with Sodium

In studying the structure of the lamellar compounds with sodium Asher and Wilson[12,60] found that graphite lines of the type 00*l* had disappeared from the Debye powder diagrams, while the graphite lines 10*l*, 112, 202, and 123 remained; i.e. the lattice parameter varied along the *c*-axis, but the structure of the carbon network of graphite remained unchanged. Indexing the X-ray diagram showed that a compound of stage (VIII) had been formed with an identity period I_C = 28 Å. On the assumption that the interplanar spacing in the unfilled graphite layer was the same (3.35 Å) as in graphite itself, the thickness of an unfilled layer was found to be I'_C = 4.5 Å (28 − 7 × 3.35). Carbon networks adjacent to sodium layers are arranged similarly (AA, BB), but the others alternate as in graphite (ABAB...). The sodium atoms in a layer are arranged in a triangular pattern, like the potassium atoms in C_8K.[6] It is not clear why the sodium atoms are most densely packed (C_8Na) in the stage (VIII) compound, whereas the packing is less compact ($C_{12}M$) in the graphite compounds of potassium, rubidium, and caesium beginning with stage (II); and in the lithium compound, beginning from stage (IV), one metal atom in a layer is associated with twelve carbon atoms from each graphite network adjacent to the lithium layer, although the atomic radius of lithium is smaller than that of sodium.

3. Structure of Binary Compounds of Graphite with Lithium

Juza and Wehle [16] found that the compounds C_6Li, $C_{12}Li$, and C_8Li all have a hexagonal crystal lattice. Table 13 gives the parameters along the a- and c-axes (I_a and I_c) together with the thickness of a filled layer (I'_c). These workers found [16] that the carbon layers are arranged in the same sequence (ABAB...) as in graphite. The carbon–carbon distance in a layer is somewhat greater than in graphite.

Table 13. Structure of lamellar compounds of graphite with lithium.

Compound	I_a, Å	I_c, Å	Stage	I'_c, Å
C_6Li	4.29_0	3.73_7	I	3.73_7
$C_{12}Li$	4.29_0	7.02_9	II	3.67_9
$C_{18}Li$	4.2_8	10.4_4	III	3.7_4

Bagouin et al. [17] have since established that the compounds— C_6Li, $C_{18}Li$, $C_{36}Li$, and $C_{72}Li$—also have a hexagonal lattice. Table 14 gives the parameters I_a and I_c together with I'_c. These authors attribute the composition $C_{18}Li$ to a compound of stage (II), and consider that the transition from stage (I) to stage (II) is accompanied by an increase in the number of carbon layers per metal layer and a decrease in the lithium content of a layer, as in the potassium compound [6]. The carbon–carbon distance in a layer is the same as in graphite.

Table 14. Structure of lamellar compounds of graphite with lithium.

Compound	I_a, Å	I_c, Å	Stage	I'_c, Å
C_6Li	4.28	3.70	I	3.70
$C_{18}Li$	7.40	7.05	II	3.70
$C_{36}Li$	—	13.75	IV	3.70
$C_{72}Li$	—	27.05	VIII	3.65

4. Structure of Graphite–Metal–Solvent Ternary Compounds

The structure of lamellar compounds of graphite with alkali metals and ammonia or amines was investigated by Rüdorff et al. [22-24], who determined the identity periods (Table 15) and established the following generalisations.

1. Intrusion of a solution of a metal into the graphite lattice yields inclusion compounds analogous in structure to those formed in the absence of a solvent (stages I, II, etc.), with the ammonia or amine molecules situated in the same layer as the metal atoms.

2. The carbon networks adjacent to a metal layer are arranged similarly, but the other networks alternate, as in the original graphite. Hence the identity period must be doubled for even stages.

3. The thickness of a filled layer in a graphite–alkali-metal–ammonia compound is 6.6 Å, and is independent of the nature of the metal (lithium, sodium, potassium, or rubidium) or the stage of the compound (I or II). It is considerably larger than the thickness of a filled layer in an alkali-metal compound containing no solvent (cf. Tables 12–14): i.e. the size of the metal atom does not affect the interplanar spacing, which is determined by the size of the solvated ion. The increase in molecular size of the solvent on passing from ammonia to methylamine and to ethylenediamine leads to an increase in thickness of the filled layer to 6.9 and 8.5 Å respectively.

Table 15. Composition and identity period I_c of alkali-metal compounds of graphite containing ammonia and amines (py = pyridine; en = ethylenediamine).

Stage I		Stage (II)	
composition	I_c, Å	composition	I_c, Å
$C_{10.6}Li(NH_3)_{1.6}$	6.6_2	$C_{28.8}Li(NH_3)_{1.7}$	9.9_3
$C_{13.4}Na(NH_3)_{2.0}$	6.6_3	$C_{26.7}Na(NH_3)_{2.3}$	9.9_7
$C_{12.5}K(NH_3)_{2.1}$	6.5_6	$C_{28.7}K(NH_3)_{2.8}$	9.9_4
$C_{11.9}Rb(NH_3)_{2.0}$	6.5_8		
$C_{12.0}Cs(NH_3)_{2.2}$	6.5_8		
$C_{12.1}Li(CH_3NH_2)_{1.9}$	6.9		
$C_{11.4}K(CH_3NH_2)_{1.0}$	6.8		
		$C_{28}Li(en)_{1.0}$	11.85=8.5+3.35
$C_{12.2}K$ (py) $_{1.0}$		$C_{20.9}K(py)_{0.84}$	

4. In the ternary graphite compounds of stage (I) one alkali-metal atom is associated with twelve carbon atoms, as in the binary lamellar compounds of stages (II)–(V). This is due to the presence of solvent molecules between alkali-metal atoms in the layer.

5. The metal atoms in the lattice are solvated, the number of solvent molecules per alkali-metal atom decreasing with increase in size of the solvent molecule (Table 15).

These conclusions have been confirmed by Ginderow and Setton's investigation [25] of the structure of the lithium and sodium compounds containing hexamethylphosphoramide $C_{32}Li.HMP$ and $C_{27}Na.HMP$. These compounds were found to be of stage (I), with the parameters

$C_{32}Li \cdot HMP$: $I_a = 19.68$ Å; $I_c = 30.48$ Å
$C_{27}Na \cdot HMP$: $I_a = 12.73$ Å; $I_c = 15.24$ Å

The alternation of carbon networks in the compound is AAA..., not ABAB... as in graphite itself. One metal atom is solvated by one solvent molecule, with the P=O bond perpendicular to the carbon lamellae. As a consequence, the thickness of a filled layer is the same in the two compounds: $I'_c = 7.62$ Å, considerably greater than for the binary compounds (4.5 and 3.7 Å) and for compounds of graphite with the alkali metals and ammonia ($I_c = 6.6$ Å). The layers of solvated atoms are displaced relative to one another. Therefore the identity period for this compound must be quadrupled: $I_c = 4 \times 7.62 = 30.48$ Å.

5. Structure of Compounds of Graphite with Alkali Metals and Oxolan

The structure of interstitial products of graphite with a metal and oxolan was investigated by Stein et al. [27-29] (cf. also Ref. 38) by means of X-rays. However, they were

unable to index the powder diagrams obtained or to determine the identity periods. From the diagrams these workers established that the products were indeed lamellar compounds, since the most characteristic lines of graphite 002 and 004 were absent (indicating a change in the identity period along the c-axis, i.e. penetration of the alkali metal between the carbon networks), while the "graphite" lines 100, 110, and 112 were present (indicating the unchanged structure of the carbon networks).

Nominé and Bonnetain [33,61] discovered that three phases were present in the lithium compound, two phases with sodium, and one phase with potassium, distinguished by their degrees of solvation. Table 16 gives the identity periods for these phases. Independently of the phase, all are stage (I) compounds. Consequently the differences in identity periods are due to differences in structure between the solvate sheaths of the alkali-metal ions. On the assumption that the thickness of a filled layer is the sum of the thicknesses of a graphite layer (3.35 Å) and a layer of solvated ions e_I, these workers calculated values of $e_I = I_c - 3.35$ (Table 16).

Table 16. Structural parameters of various phases in graphite–alkali-metal–oxolan compounds.

Phase	I_c, Å	e_I
φ_1(Li)	7.24	3.89
φ_2(Li)	12.45	9.10
φ_3(Li)	17.2	13.85
φ_1(Na)	7.24	3.89
φ_2(Na)	11.12	7.77
φ_1(K)	7.18	3.88

The use of models to study the structure of the solvated ions showed that, in the phases φ_1(Li), φ_1(Na), and φ_1(K), the oxolan molecules are oriented parallel to the plane of the graphite. Each alkali-metal layer is surrounded by three oxolan molecules. In the phases φ_2(Li) and φ_2(Na) a metal ion is surrounded by four oxolan molecules located at the vertices of a tetrahedron. With lithium the tetrahedron is regular, but in the case of sodium it is somewhat flattened between two graphite layers. In the phase φ_3(Li) the lithium ion is surrounded by oxolan molecules at the corners of an octahedron, a diagonal of which, like the planes of the oxolan molecules, is perpendicular to the graphite layers.

V. PHYSICAL PROPERTIES AND NATURE OF BONDING

1. Electrical Conductivity of Compounds of Graphite with Alkali Metals

The electrical conductivity of alkali-metal lamellar compounds has been investigated only on binary systems [7,10,62–69,74]. Since detailed discussions of the results will be found in reviews [70–72], we shall consider here only the main conclusions.

1. Incorporation of an alkali metal into graphite leads to an increase in the conductance of the latter, by factors of 10 and 200 along the a- and c-axes respectively.

2. Alkali-metal complexes of graphite exhibit a considerable positive temperature coefficient of the resistance.

3. Increase in the potassium content is accompanied by a continuous fall in resistance along the c-axis, whereas the resistance reaches a limit along the a-axis at compositions far removed from saturation [62].

It is interesting that similar generalisations apply to the solid alkali-metal compounds of aromatic hydrocarbons [73,74]. Thus the solid complexes of anthracene with lithium, sodium, and potassium have a considerable positive temperature coefficient of resistance. The graphite compounds C_8M (where M = K, Rb, Cs) are superconductors [63,75], their superconductivity appearing at 0.55°, 0.151°, and 0.135°K respectively. The compound $C_{24}K$ is not a superconductor, which was explained on the assumption that only every other interlayer space was occupied by potassium. However, Salzano and Strongin have since shown [63] that this may be due to a decrease in the potassium content of a layer on passing from C_8K to $C_{24}K$.

Table 17. Magnetic susceptibilities of graphite, potassium, and their lamellar compounds (χ_m calculated as 10^{-6} c.g.s. g-atom^{-1} C).

Material	90° K		195° K		288° K		Bulk density, g cm^{-3}
	χ_s	χ_m	χ_s	χ_m	χ_s	χ_m	
K	+0.540	+21.1	+0 538	+21.0	+0.539	+21.1	0.849
Graphite	−7.909	−94.81	−6.757	−81.08	−6.04	−72.48	0 783
$KC_{8.47}$	+1.01	+16.78	+1.01	+16.78	+1.00	+16.61	0.730
$KC_{7.79}$	+0.953	+16.23	+0.951	+16.17	+0.953	+16.23	0.713

2. Magnetic Susceptibility of Lamellar Compounds of Graphite with Alkali Metals

Measurements of the magnetic susceptibility of lamellar compounds of graphite with potassium [10,76–78] showed that intercalation of the metal had replaced the abnormally high diamagnetism of graphite by weak paramagnetism, which remained unchanged when the compound was treated with liquid ammonia. McDonnel et al. [10] found that the paramagnetism of these lamellar compounds exceeded the additive value calculated from the contributions of potassium and of graphite. However, the paramagnetism is independent of temperature, like the susceptibility of potassium (Table 17), and cannot be explained by the presence of isolated potassium atoms, whose susceptibility would be inversely proportional to the temperature. Rüdorff et al. [6,23,24] found that the susceptibility of lamellar compounds of graphite with potassium and with rubidium of stages (I)–(V) was strongly dependent on the field strength. Comparable values (Table 18) were obtained by extrapolating the results to H_∞. In contrast to previous papers, these workers showed that the paramagnetism of the compounds diminished with fall in temperature. No explanation was given for this fact. Measurement of the magnetic susceptibility of the sodium compound has shown [15] that the diamagnetism of graphite decreases with increase in the sodium content (Fig. 5), and completely disappears when 1.95% of sodium, corresponding to the composition $C_{96}Na$, has been incorporated.

The electron spin resonance spectra of compounds of graphite with lithium, sodium, and potassium [76] prepared from solutions of the metals in liquid ammonia showed

that the line width was unaffected by the presence of ammonia. Furthermore, the relaxation time was found to be of the same order as predicted by theory for metallic conductors. The metallic character of the bond in the compounds was confirmed also by the temperature dependence of the line width (Table 19).

Table 18. Magnetic susceptibility of lamellar potassium and rubidium compounds at 295°K.

Stage	Potassium compounds		Rubidium compounds	
	composition	$10^6\chi_{mol}$	composition	$10^6\chi_{mol}$
Graphite		−110		−110
I	$CK_{0.120}$	+10.0	$CRb_{0.119}$	+5.0
II	$CK_{0.037}$	+8.7	$CRb_{0.040}$	+5.1
III	$CK_{0.027}$	+8.5	$CRb_{0.028}$	+5.6
IV	$CK_{0.021}$	+5.7	$CRb_{0.019}$	+6.2
V	$CK_{0.015}$	+4.0	$CRb_{0.014}$	+3.7

Ginderow and Setton [25] examined the e.s.r. spectra of the lithium and sodium compounds with hexamethylphosphoramide (HMP), and detected a signal. With H = 280 Mc/s the g-factor and the line width were found to be

$C_{32}Li \cdot HMP$ $g = 2.0023$ $\Delta H = 0.470$ G
$C_{27}Na \cdot HMP$ $g = 2.0023$ $\Delta H = 0.436$ G

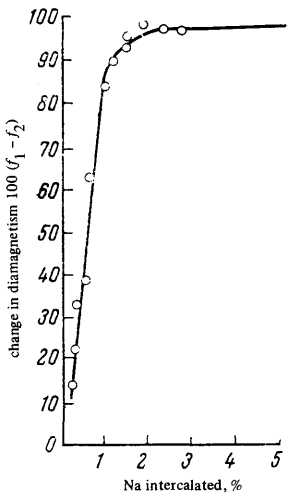

Figure 5. Dependence of diamagnetism of graphite on quantity of intercalated sodium.

The calculated spin densities of the lithium and sodium compounds were respectively 2.1×10^{22} and 7.0×10^{22} spins mole^{-1}. On the assumption that the spin density was due solely to unionised atoms, these workers calculated the percentage of unionised metal as respectively 4% and 15% for lithium and for sodium. They investigated also [35] the e.s.r. spectra of the inclusion products obtained by the action of a solution of sodium or potassium benzophenone ketyl on graphite (Table 20), and obtained rather different contents of unionised metal (9% with sodium, and 6% with potassium).

Table 19. Line widths in e.s.r. spectra of alkali-metal lamellar compounds.

Metal	ΔH_1 (300°K), mG	ΔH_2 (77°K), mG
Li (conc.)	100	70
Li (dil.)	86	60
Na	115	77
K[a]	350[b]	—
K	275	275

[a] Compound obtained in a vacuum; it contains no ammonia.
[b] Measured at 425 Mc/s.

However, Rose et al. [79] suggested that the signals in the e.s.r. spectra were due, not to compounds of graphite with alkali metals, but to complexes of the latter with aromatic hydrocarbons which had penetrated the graphite. They examined [79] the e.s.r. spectra of inclusion products obtained by the action of oxolan solutions of the lithium, sodium, and potassium derivatives of naphthalene, and found that the paramagnetism of all the compounds disappeared irreversibly when they were heated in a vacuum to 180–300°C. This was accompanied by separation of all the oxolan and a small quantity of naphthalene from the compound (Fig. 6). Values of the g-factor close to 2 were obtained for the different graphite compounds—2.0023, 2.0028, and 2.0023 for lithium, sodium, and potassium respectively—which are characteristic of the free radical-anion of naphthalene (g = 2.0026) (Table 21).

Table 20. Data on e.s.r. spectra of alkali-metal lamellar compounds obtained from benzophenone ketyls and graphite.

Property	Compound	
	$NaOxC_{64}$	$KOxC_{12}$
ΔH, G	~1.3	~2.5
g-factor	1.999	1.997
Spins g^{-1}	$6.21 \cdot 10^{19}$	$3.44 \cdot 10^{19}$
Spins mole^{-1}	$5.34 \cdot 10^{22}$	$3.41 \cdot 10^{22}$
Unionised metal, %	8.9	5.7

The graphite complexes are relatively insensitive to traces of water vapour. This is regarded [79] as indicating that the complex of naphthalene with the alkali metal is not simply adsorbed on the graphite but enclosed between its planes. The absence of hyperfine splitting in the spectra of these compounds is explained by the absence of free movement of the naphthalene molecules enclosed between the graphite planes.

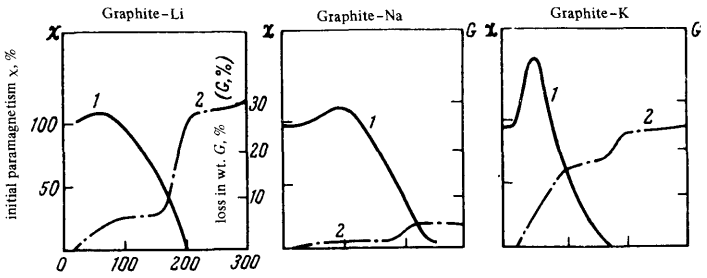

Figure 6. Dependence of paramagnetism of alkali-metal lamellar compounds on temperature of specimen: 1) paramagnetism; 2) loss in weight (oxolan, naphthalene).

3. Nature of Bond in Lamellar Compounds of Graphite with Alkali Metals

Salzano and Aronson have proposed a model [9,41-44], representing the type of bonding in lamellar compounds of graphite with potassium, rubidium, and caesium, in which the compounds comprise "metallic" carbon networks and layers of metal ions M^+. They suggest that a positive ion is formed by transfer of an electron from a metal atom to the conduction band of an adjacent graphite layer. Thus the metal atoms in the lamellar compounds are completely ionised, and the bond between the alkali metal and the carbon network is formed by electrostatic interaction of positive metal ions with free electrons in the conduction band of adjacent graphite layers, as in the bond between metal ions and aromatic radical-anions and dianions. This model is supported by the facts indicated below.

Table 21. Data on e.s.r. spectra of alkali-metal lamellar compounds prepared from radical-anions of naphthalene and graphite.

Parameter	Proportion of spins of various compounds		
	$C_{18}LiOx_{1.4}\cdot Naph_{0.020\pm0.010}$	$C_{50}NaOx_{0.6}\cdot Naph_{0.10\pm0.005}$	$C_{24}KOx_{1.6}\cdot Naph_{0.003}$
10^{-19} spins g^{-1}	2.1 2.5 2.5 —	— 0.9 0.4 —	0.2 0.4 0.6 1.6
10^{-19} spins g^{-1} based on naphthalene	3.7 ± 1.8	0.9 ± 0.4	0.4 ± 0.25
g-factor	2.0029 2.0028	2.0027 2.0029	2.0021 2.0025

1. The lamellar compounds of graphite with alkali metals are more highly conducting than graphite itself [7,10], and those of composition C_8M are even superconducting [75].

2. The resistance of the compounds has a positive temperature coefficient [69-71]. A similar relation is observed with the solid alkali-metal compounds of aromatic hydrocarbons [72,73].

3. Investigation of the optical properties of the compounds has revealed [80] that electrons are transferred from the alkali metal to the carbon networks.

4. The Mössbauer spectra of the caesium compounds indicate [81] that the metal in them is completely ionised.

5. Calculations by Setton show [82] that the interplanar spacing in a filled layer is the sum of the radii of the metal ions M^+ and the van der Waals thickness of a carbon layer.

6. The thickness of a filled layer is the same for compounds of different stages.

This model enabled Salzano and Aronson [43,44] to explain the variation in the heat and entropy of decomposition of the lamellar compounds with potassium, rubidium, and caesium. According to Table 8 the formation of C_8M from $C_{10}M$ is accompanied by the largest heat effect, since work must be done, in all stages other than (Ib), to increase the separation between the carbon networks from 3.35 Å (in the original graphite) to 5.4–6.0 Å (in the alkali-metal compounds) so that metal is able to penetrate into the space between the planes. The formation of C_8M from $C_{10}M$ does not require the separation of graphite planes, since in $C_{10}M$ all the planes are already separated. The compound C_8M is formed by the incorporation of additional M atoms into each layer. Therefore the heat evolved in the formation of C_8M from $C_{10}M$ exceeds the heat of formation of other phases by the work required to move the carbon layers apart from 3.35 to 5.4–6.0 Å. The increased heats of formation of compounds from $C_{10}M$ to $C_{60}M$ was explained by these workers by a diminution in the repulsion between adjacent layers of metal ions, since they are separated by increasing numbers of carbon layers. On the basis of this model they used a Born–Haber cycle to calculate the energy of bonding of caesium with graphite in the lamellar compounds [42] as between −67 and −55 kcal g-atom^{-1} Cs, in agreement with the value found from thermodynamic data (55 kcal mole g-atom^{-1} Cs).

Calculation of the thermodynamic stability of the caesium compounds of various stages has shown [40] that the phases—$C_{24}M$ (stage II), $C_{36}M$ (III), $C_{48}M$ (IV), and $C_{60}M$ (V)—should be the most stable. For stage (I), however, the model predicts that the phases $C_{12}M$, $C_{16}M$, and $C_{20}M$ should be more stable by an order of magnitude than C_8M and $C_{10}M$. Thus the proposed model represents correctly the composition, the structure, and the nature of the bond in compounds from $C_{24}M$ to $C_{60}M$. Yet it is of little use for compounds C_8M and $C_{10}M$ (*a*) repulsion between adjacent layers of metal ions should be strongest for these compounds, since they are separated by only one carbon network, so that C_8M should have the smallest heat of formation, which is contrary to the experimental result; (*b*) this model does not predict the stability of these compounds C_8M and $C_{10}M$, although it has been shown experimentally that C_8M—not $C_{12}M$ or $C_{16}M$—is formed; and (*c*) heats of formation of C_8M and $C_{10}M$ from the elements, calculated on the basis of models, differ substantially from the experimental values [40].

Nevertheless, the suggested model provides a qualitative explanation of the fact that lamellar compounds are formed either with difficulty or not at all by the direct reaction of lithium and sodium vapours with graphite. According to the views of McDonnel et al.[10] the incorporation of an alkali metal into graphite can be represented by the scheme

$$K_{gas} \rightarrow K^+_{gas} + [\bar{e}];\ \Delta H_1 = +101{,}1$$
$$[\bar{e}] + [C]_{lamell} \rightarrow [C]^-_{lamell}$$
$$K^+_{gas} + [C]_{lamell} \rightarrow C_8K + \Delta H_2$$
$$K_{gas} + [C]_{lamell} \rightarrow C_8K + \Delta H;\quad \Delta H = \Delta H_2 + 101{,}1$$

The calculated value of ΔH_2 is -126 kcal g-atom^{-1} K. These authors assume that the energy evolved (ΔH_2) is necessary to balance the ionisation energy of potassium. In view of the ionisation potentials of the alkali metals, they consider that the energy evolved in the third stage is sufficient for the formation of compounds of graphite with potassium, rubidium, and caesium, and insufficient to form the compounds C_8Li and C_8Na. Since Salzano and Aronson's model is similar to that of the alkali-metal compounds of aromatic hydrocarbons, solvation may be supposed to be the additional energetic factor favouring the formation of lamellar compounds with lithium and sodium. Indeed, results obtained by Rüdorff[22-24] and also by Ginderow and Setton[25] show that lithium and sodium atoms, solvated by ammonia, amines, or hexamethylphosphoramide, penetrate graphite at $-50°$ and 20°C respectively, to form stage (I) compounds.

VI. CHEMICAL PROPERTIES

Little information has been published on the chemical properties of the alkali-metal lamellar compounds. Rüdorff[6] reported that hydrogen was evolved by the action of water on the potassium, rubidium, and caesium compounds. Hydrogen is evolved also by the action of water on the compounds of graphite with lithium[16,17], on the ternary compounds with an alkali metal and oxolan[27,31], and on the ternary compounds containing lithium, potassium, or sodium and ammonia[24]. It is interesting that hydrogen is evolved also when these graphite complexes are heated, amides of the alkali metals being formed[24]. In none of these cases was the quantity of hydrogen determined, although it may be expected (from the similarity between the alkali-metal lamellar compounds and aromatic radical-anions) that the graphite will be hydrogenated by the action of water.

Saehr and Hérold[83-85] have shown that the compound C_8K absorbs hydrogen slowly even at room temperature, the reaction being accelerated by heating. Products C_8KH_x are formed in which x varies with temperature to a limiting value of 0.67. The compounds of C_8Rb and C_8Cs are less active than C_8K: the maximum value of x in C_8RbH_x is 0.05, reached at 60°C; C_8Cs does not react with hydrogen between $-78°$ and +150°C. The compound $C_{24}K$ absorbs hydrogen to form $C_{24}KH_{0.25}$. Investigation of the structure of $C_8KH_{0.67}$ by the Debye–Scherrer method showed that the lines corresponding to C_8K had disappeared, while potassium hydride and graphite phases were not formed. The powder photographs contained distinct lines due to a new phase with identity periods I_c = 11.9 Å and I_a = 4.92 Å. The authors give no interpretation of this structure. The heat of sorption of hydrogen is found to be 8.1 kcal g-atom^{-1} K for the compound C_8K. Although C_8Cs does not absorb hydrogen[84], this compound catalyses the isotopic exchange of hydrogen with deuterium and the conversion of *ortho*-hydrogen into *para*-hydrogen[86].

According to Diebold and Hérold[87,88] gaseous chlorine and also the vapours of bromine and iodine react very vigorously with C_8K and C_8Cs to form the metal halides, the structure of the lamellar compound being completely destroyed. X-Ray examination shows that the product comprises a graphite phase and a metal-halide phase. Almost all the salt can be washed out with water. Thermogravimetric results show[89] that the salt in the graphite melts at the same temperature as the pure salt.

In 1969 it was reported[90] that oxygen and carbon monoxide react with C_8K to form a KO_2 or K_2CO_3 phase mixed with graphite. According to Sudo et al.[91] C_8K absorbs nitrogen at room temperature.

Jensen et al.[92] demonstrated the reducing properties of C_8K in its reaction with bis(trialkyl phosphite)nickel(II) dichlorides and excess of the trialkyl phosphite to form a zerovalent nickel complex—tetrakis(triethyl phosphite) nickel(0).

The alkali-metal lamellar compounds catalyse the polymerisation of alkenes[84,93-96], the isomerisation of alkenes[97], and also the alkylation by alkenes of benzene derivatives in the ring and in the side-chain[98]. With ethylene at 1000 atm on C_8K at 200°C the products are C_8–C_{14} *trans*-monoalkenes together with a small quantity of a solid polyethylene of low molecular weight[93]. Greater catalytic activity is found with C_8K than with pure potassium dispersed in its chloride or oxide. According to Hambling and Alderson[95] treatment of the compounds—C_8K, $C_{16}K$, $C_{24}K$, $C_{36}K$, $C_{48}K$, $C_{60}K$, and $C_{64}K$—with alkyl or aryl halides and halides of transition metals (titanium, zirconium, vanadium, chromium, molybdenum) modifies them in such a way that the products catalyse the polymerisation of ethylene, propene, and butene at 50–250°C with the formation of products of high molecular weight. The rate of polymerisation of styrene on C_8K and $C_{24}K$ is lower[94], but the molecular weight of the polymer is higher, than in the presence of pure, finely divided potassium.

Golé and Stein[96] have shown that $C_{32}K$ also catalyses the polymerisation of styrene in various solvents (oxolan, benzene, cyclohexane, hexane, carbon tetrachloride) at 25–30°C. In the polymerisation of dienes—butadiene and isoprene[94,96,99]—on C_8K, $C_{24}K$, and $C_{32}K$, the mode of addition is 1,2 and *trans*-1,4 with the former compound, and 1,2, *trans*-1,4, and 3,4 with isoprene. No *cis*-1,4-addition product is formed.

In 1958 Podal and Foster[98] discovered that C_8K catalyses not only the polymerisation of ethylene but also the alkylation of benzene and toluene in the ring and in the side chain. With ethylene at 700 atm and 110°C benzene yields 2-butylbenzene (35%), dialkylbenzenes, and higher monoalkylbenzenes. Ethylbenzene was not detected. These results are opposite to those obtained with organosodium compounds as catalysts[100]. Raising the temperature to 200°C leads to the formation of biphenyl (19%) together with s-butylbenzene (23%). The appearance of biphenyl was attributed to dimerisation of benzene radical-anions formed from benzene and the graphite–potassium complex. The reaction between toluene and ethylene yields triphenylpentane (at 120°C) or n-propylbenzene (55°C). t-Pentylbenzene is formed from isopropylbenzene (200°C).

Ottmers and Rase[97] studied the isomerisation of pent-1-ene into *cis*- and *trans*-pent-2-enes in the presence of

C_8K, $C_{24}K$, $C_{36}K$, $C_{48}K$, and $C_{60}K$ at temperatures between 75° and 235°C. They found that the reaction velocity and the *trans/cis* ratio increased with rise in temperature. At a given temperature the activity of the catalysts varied in the sequence—$C_{60}K > C_{48}K > C_{36}K > C_{24}K > C_8K$. The activity of the catalyst decreases during the reaction, and this decrease is more rapid the higher the temperature.

Comparison of the catalytic activity of these compounds with that of an industrial aluminosilicate catalyst [97] shows that the potassium complex of graphite is more active at low temperatures, and the aluminosilicate catalyst at high temperatures.

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The Chemistry of Trialkyloxonium Fluoroborates

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The preparation and the chemical properties of trialkyloxonium fluoroborates—highly effective alkylating agents—are surveyed. Special attention is paid to the *O*-alkylation of organic compounds (ethers, epoxides, oxo- and hydroxy-derivatives, *N*-oxides, etc.). The bibliography contains 104 references.

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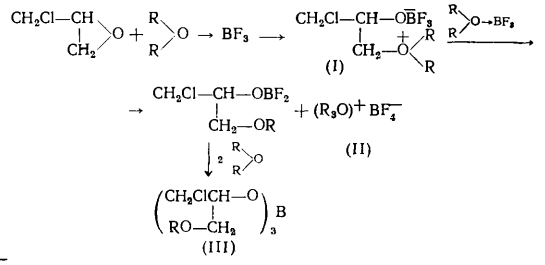
I. INTRODUCTION

The discovery in 1937 by Meerwein and his coworkers[1] of a new class of highly effective alkylating agents—trialkyloxonium salts—considerably extended the field of application of alkylation reactions in organic chemistry. In the course of the investigation of tertiary oxonium salts methods were developed for the preparation of hitherto unknown classes of organic compounds, such as acetals of amides, lactams, and lactones, azidinium salts, etc. New and more effective procedures were found for obtaining known types of compounds (e.g. imidic esters, orthoesters, lactimidic esters, etc.). Among the large number of trialkyloxonium salts which have now been obtained, trimethyloxonium and triethyloxonium fluoroborates have found the widest use in preparative organic chemistry. A considerable number of interesting investigations have been made during recent years on the use of these alkylating agents for the preparation of complicated organic compounds, the results of which do not appear in Meerwein's brief review[2] of the chemistry of various types of oxonium salts. The present Review summarises available information on the synthetic application of trialkyloxonium fluoroborates, primarily the trimethyloxonium and triethyloxonium salts†.

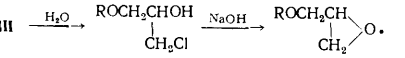
II. PREPARATION OF TRIALKYLOXONIUM FLUOROBORATES

The most widely used method for preparing trialkyloxonium fluoroborates is based on the reaction between 2-chloromethyloxiran and the appropriate ether complex of boron trifluoride in excess of the ether[1,4]:



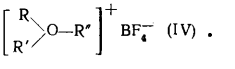
† The Review does not include information on triaryloxonium salts[3], nor on the applications of trialkyloxonium salts in the chemistry of macromolecular compounds.

The above mechanism is supported by the isolation of intermediate inner salts of type (I: R = CH_3, C_2H_5), and the fact that (I: R = C_2H_5) gives triethyloxonium fluoroborate (II: R = C_2H_5) with diethyl ether and its boron trifluoride complex. The boric esters formed in this reaction can be converted into 2-alkoxymethyloxirans:

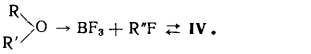


The latter in turn are able to give trialkyloxonium fluoroborates[5].

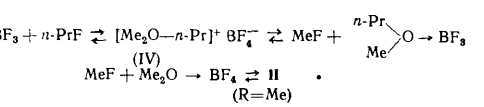
The above method can be used to prepare trimethyloxonium and triethyloxonium fluoroborates (II: R = CH_3, C_2H_5). However, when R = n-C_3H_7, the yield of (II) does not exceed 30%, and oxonium salts containing higher alkyl radicals could not be obtained at all. Furthermore, it is evident from the above scheme that this method cannot be used to prepare unsymmetrical oxonium salts of the type



Such oxonium salts can in principle be obtained by the reaction of alkyl fluorides with the ether complexes of boron trifluoride[3]:



Thus the corresponding oxonium salts are obtained in satisfactory yields by keeping the reactants in a sealed tube for a long time. The compounds (II: R = C_2H_5), (IV: R = R′ = CH_3; R″ = C_2H_5), and (IV: R = R′ = C_2H_5; R″ = CH_3) have been prepared by this method. However, the method is not universally applicable to the preparation of salts of type (IV). For example, reaction between the dimethyl ether complex of boron trifluoride and propyl fluoride yields merely (II: R = CH_3) instead of the expected (IV: R = R′ = CH_3; R″ = n-C_3H_7):

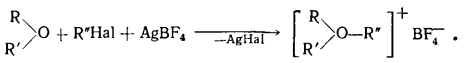


Evidently formation of the more symmetrical cation is energetically more favourable in this reaction. The above scheme agrees well with the easier elimination of methyl rather than other alkyls from the cations (see

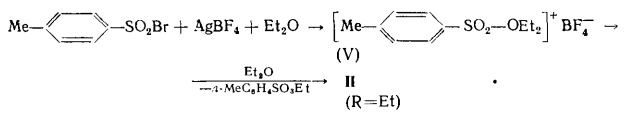
Section III). The formation of (II: R = CH_3) is seen to be based on a series of reversible reactions. The decomposition of triethyloxonium fluoroborate when heated above the melting point provides evidence that oxonium salts are in equilibrium with the alkyl halides and the ether complexes of boron trifluoride: the diethyl ether complex and ethyl fluoride were isolated in high yields[1].

Although the above method enables various oxonium salts (including unsymmetrical salts) to be obtained, the considerable duration of the process (several months) and the relatively low yields make it unsuitable for practical preparations.

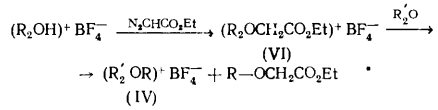
Trialkyloxonium fluoroborates can be prepared more conveniently by the reaction of alkyl halides with ethers in the presence of silver fluoroborate[6,7]:



This reaction can be used to obtain not only trialkyloxonium but also mixed acylalkyloxonium salts. For example, treatment of a mixture of ether and silver tetrafluoroborate with toluene-*p*-sulphonyl bromide at −70°C gives the corresponding oxonium salt (V), from which triethyloxonium fluoroborate (II: R = C_2H_5) is obtained on further reaction with ether[8]:



Trialkyloxonium fluoroborates can be prepared also by the reaction of dialkyloxonium fluoroborates with diazomethane or with ethyl diazoacetate[9]



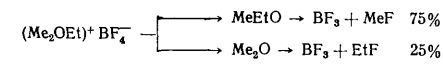
The oxonium salt (VI) formed in the first stage of the reaction is further alkylated by an ether molecule to give the tertiary oxonium salt (IV).

The reaction of a trialkyloxonium fluoroborate with an ether, which is discussed in Section IIIA, 1, provides another method for the preparation of trialkyloxonium fluoroborates.

III. PROPERTIES AND REACTIONS OF TRIALKYLOXONIUM FLUOROBORATES

Trialkyloxonium fluoroborates, like ammonium salts, are typical ionic compounds, whose solutions in anhydrous sulphur dioxide are electrically conducting[4]. They are readily soluble in polar solvents such as nitrobenzene, nitromethane, anhydrous sulphur dioxide, etc. Their solubility in less polar solvents is determined by the length of the alkyl radicals: "loading" the hydrophobic alkyl radicals produces an increase in solubility in these solvents, so that e.g. (II: R = C_2H_5) dissolves well in dichloromethane, whereas (II: R = CH_3) is almost insoluble. All the lower oxonium fluoroborates are solids which melt with decomposition; their melting points fall regularly with increase in length of the alkyl[1,4].

A characteristic property of tertiary oxonium salts is their dissociation at high temperatures with the separation of ether complexes of boron trifluoride and alkyl fluorides. Methyl is detached more readily than other alkyl radicals. For example, the decomposition of ethyldimethyloxonium fluoroborate when heated above 120°C occurs as follows[1]:

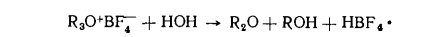


Trialkyloxonium salts decompose not only at high temperature but also when their solutions are allowed to stand. In particular, triethyloxonium fluoroborate is unstable in solution, decomposing comparatively readily into diethyl ether, boron trifluoride, and ethyl fluoride[10]. Decomposition is accelerated by the addition of ethers to the solutions[10].

A. *O*-ALKYLATION BY TRIALKYLOXONIUM FLUOROBORATES

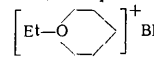
1. Reactions with Hydroxylated Compounds, Ethers, and Epoxides

The simplest and most thoroughly studied reaction of this type is the hydrolysis of tertiary oxonium salts[1]:

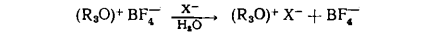


Hydrolysis is accompanied by the formation of an alcohol and an ether, so that the electrical conductivity of the solutions falls gradually[4]. Table 1 gives the rate of hydrolysis of several salts, determined from the variation in the conductivity of aqueous solutions[4]. The results show that "loading" the alkyl radicals, as well as including positively charged oxygen in a ring, leads to considerable stabilisation of tertiary oxonium salts towards water.

Table 1. Times (min) for complete hydrolysis (at 18°C).

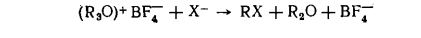
$(Me_3O)^+BF_4^-$	8
$(Et_3O)^+BF_4^-$	80
$(n\text{-}Pr)_3O^+BF_4^-$	120
	220

The relatively low rate of hydrolysis enables ion exchange to be effective with the formation of water-insoluble oxonium salts containing complex anions[4]:



where R = CH_3, C_2H_5; X = $AuCl_4$, $SnCl_4$, HgI_3, $SbCl_6$, etc. Double decomposition of (II: R = C_2H_5) with sodium tri-iodomercurate can be used for the quantitative determination of triethyloxonium fluoroborate[4]. Similarly, the reaction of (II: R = CH_3, C_2H_5) with 2,4,6-trinitrobenzenesulphonic acid yields the corresponding trinitrobenzenesulphonates, which also serve as alkylating agents[11].

When nucleophilic agents other than the hydroxide ion are present in aqueous solution, two competing processes—hydrolysis of the salts and formation of RX



may occur. Table 2 gives the yields of ethylation products obtained when various anions react with triethyloxonium fluoroborate in water[3]. It is evident that the yields of alkylation products usually increase with increase in the polarisability of the anion[4].

Trialkyloxonium fluoroborates react with hydroxylated compounds such as alcohols, phenols, and carboxylic acids with formation of the corresponding *O*-alkyl derivatives[1,2] (a reaction similar to hydrolysis or the ethylation of anions):

$$(R_3O)^+ BF_4^- + R'OH \rightarrow RO_2 + HBF_4 + R'OR \ .$$

Use of the sodio-derivatives of the hydroxylated compounds (i.e. alkylation of the anion $R'O^-$) increases the yields of alkylated products owing to the considerable increase in electron density on the oxygen atom[1,2].

Table 2.

X⁻	F⁻	Cl⁻	Br⁻	I⁻	CNS⁻	CN⁻
Yield of C_2H_5X, %	trace	12	23	53	64	55

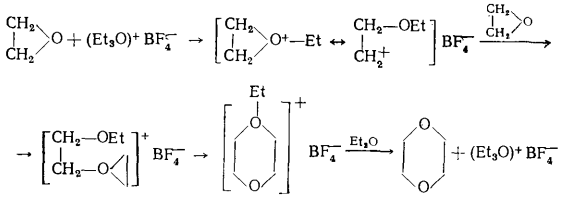
The alkylation of alcohols, phenols, and carboxylic acids does not in all cases, of course, require the use of such strong alkylating agents as trialkyloxonium salts. However, where mild conditions are necessary (e.g. in stereospecific synthesis) or when other methods of alkylation give low yields of the desired products, the application of tertiary oxonium salts acquires considerable preparative value. For example, triethyloxonium fluoroborate is employed for the ethylation of chloroalkanols[1,2] (these compounds cannot be alkylated in alkaline medium[1,2] owing to the elimination of hydrogen chloride with formation of an epoxide) and for the alkylation of (+) (*S*)-pinacolyl alcohol[12].

The alkylation of ethers occupies a special position among the reactions of trialkyloxonium fluoroborates, since it results in new oxonium salts[2]:

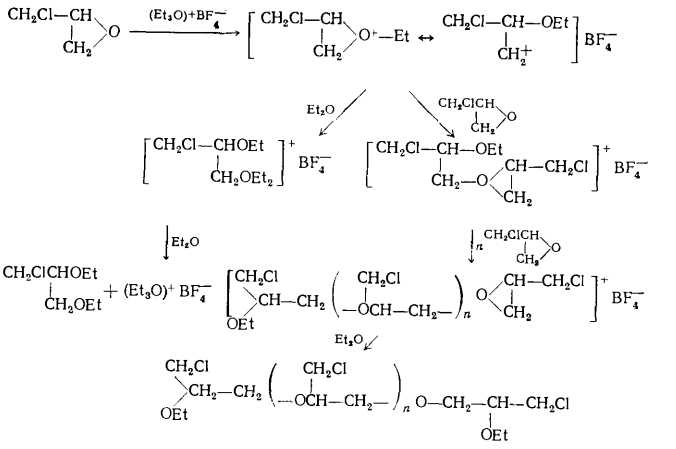
$$(R_3O)^+ BF_4^- + R'_2O \rightleftarrows (R'_2OR)^+ BF_4^- + R_2O \ .$$

As the reaction between oxonium salts and ethers is reversible, the yield of newly formed fluoroborates depends both on the stability of initial and final salts and on their solubility in the reaction medium. In the reaction of (II: R = C_2H_5) with dimethyl ether, for example, a 92% yield of (II: R = CH_3) is formed, whereas in the reaction of the same salt with oxan the yield of ethyloxanium fluoroborate is only 52%.

The first stage in the reaction of trialkyloxonium fluoroborates with epoxides[13] resembles their reaction with ethers. However, the subsequent reactions of the resulting oxonium compounds depend on the structure of the initial epoxide. Thus dioxan has been isolated as final product of the reaction of triethyloxonium fluoroborate with oxiran in ether[13]:



With chloromethyloxiran reaction can occur in two ways[13]:



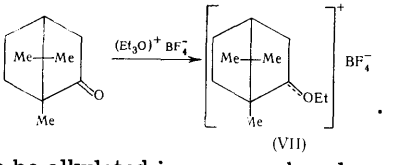
products of different degrees of polymerisation being formed depending on the reaction conditions.

2. Reactions with Carbonyl Compounds

A detailed study of reactions of this type enabled Meerwein et al.[14] to arrange carbonyl compounds in the following sequence according to their capacity for alkylation by oxonium salts: aldehydes < ketones < esters < lactones < acid amides < lactams. This sequence will be adopted in the present survey.

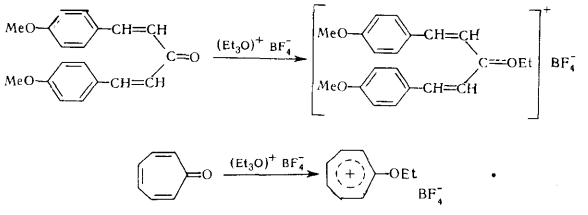
(*a*) Alkylation of aldehydes, ketones, and carboxylic esters

The reaction of aldehydes and ketones with tertiary oxonium salts yields only aldol condensation products[2]: owing to the low basicity of these compounds, they do not usually undergo *O*-alkylation. In some cases, nevertheless, alicyclic ketones are alkylated, and camphor, for example, gives the corresponding fluoroborate (VII) in 78% yield[1]:



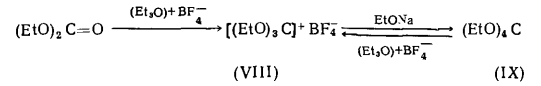
(VII)

The ability to be alkylated increases sharply on passing from simple to $\alpha\beta$-unsaturated ketones, as a consequence of the considerable stabilisation of the resulting cation. Quantitative yields are obtained, for example, in the reactions of triethyloxonium fluoroborate with di-*p*-methoxystyryl ketone[1] and with tropone[15]:



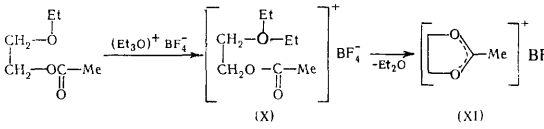
In esters, as in saturated aldehydes and ketones, the electron density on the carbonyl is usually insufficient for

alkylation by oxonium salts[2]. When, however, the resulting cation is largely stabilised by conjugation, as e.g. in the ethylation of carbonic ester, it is possible to obtain the corresponding fluoroborate salt (VIII)[16], whose structure has been proved by conversion into tetraethoxymethane (IX):



(VIII) (IX)

Alkylation of ethers occurs appreciably more readily than that of carbonyl compounds. When the molecule contains both functions, e.g. 2-ethoxyethyl acetate, the first stage is *O*-alkylation of the ether[14]:

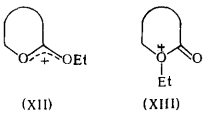


(X) (XI)

The resulting cation (X) is stabilised by elimination of a molecule of ether with the formation of 2-methyl-1,3-dioxolenium fluoroborate (XI).

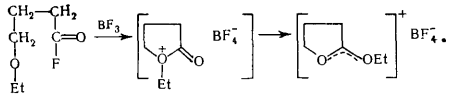
(*b*) Alkylation of lactones

Trialkyloxonium fluoroborates alkylate lactones solely at the carbonyl oxygen[16]. The explanation of such selectivity is that the resulting cation (XII) is stabilised by conjugation, unlike the cation (XIII), which might have been obtained by alkylation of the cyclic oxygen atom.

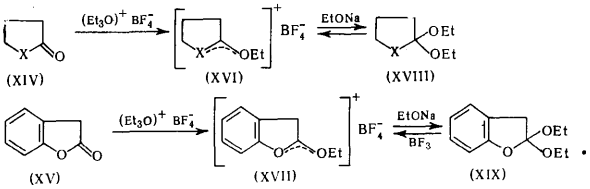


(XII) (XIII)

If, however, only cations of type (XIII) can be formed, they immediately pass into stabilised cations of type (XII)[16]:



Examples of the reaction of triethyloxonium fluoroborate with lactones are provided by the alkylation of compounds (XIV: X = O, S) and phthalide (XV)[17]:

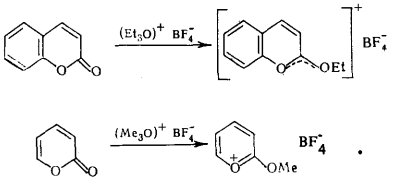


(XIV) (XVI) (XVIII)

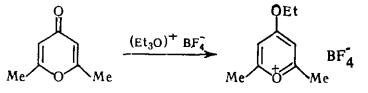
(XV) (XVII) (XIX)

Treatment of the salts (XVI) and (XVII) with sodium ethoxide converts them into lactone acetals (XVIII) and (XIX)[16].

Lactones which can form fluoroborates with stable cations are especially readily alkylated[1,18]:

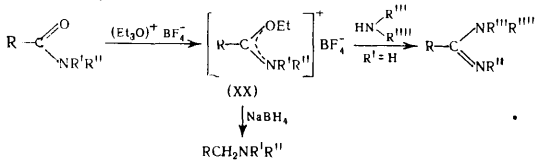


Similarly, the action of triethyloxonium fluoroborate on 2,6-dimethyl-4-pyrone readily forms the stable 4-ethoxy-2,6-dimethylpyrylium fluoroborate[1]:



(*c*) *O*-Alkylation of amides

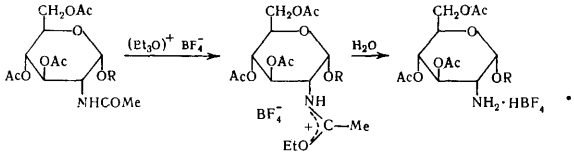
The reaction of trialkyloxonium fluoroborates with compounds containing an amide function is one of the most promising for synthetic purposes. It is sufficient to note that this reaction has opened up a new pathway for the preparation of such important and extremely reactive compounds as imidic and lactimidic esters[18]. Several members of a new class of organic compounds—amide and lactam acetals—have also been synthesised[19-21]. Meerwein first accomplished the reaction of trialkyloxonium fluoroborates with amides and lactams in the case of acetamide[1], and subsequently extended the reaction to a large number of diverse compounds containing an amide function[16,20]. The salts of imidic esters formed by alkylation are easily converted by amines into amidines[22]:



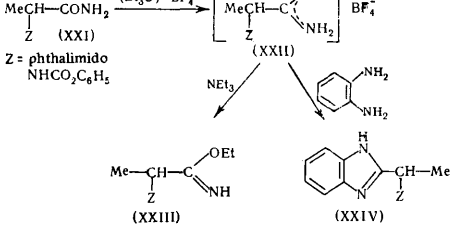
(XX)

Fluoroborates of imidic esters (XX) can be reduced by sodium tetrahydroborate under mild conditions to give high yields of the corresponding amines[23]. Since amides are usually reduced by means of the considerably less selective lithium tetrahydroaluminate, the new method shows great promise for the preparation of various amines, including polyfunctional compounds, which are difficult to obtain by other methods.

The availability of salts of type (XX) also provides opportunities for the selective detachment of *N*-acyl groups under exceptionally mild conditions, for salts of imidic esters are easily hydrolysed by water. This has been utilised for removing a protective *N*-acetyl group while preserving acetoxy-groups[24]:

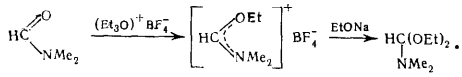


In substituted alaninamides (XXI) only the carbamoyl group is affected by triethyloxonium fluoroborate, in spite of the simultaneous presence of a phthalimido- or a phenoxycarbonylamino-group. The structure of the resulting fluoroborates (XXII) was proved by converting them into imidic esters (XXIII) and substituted benzimidazoles (XXIV)[25]:

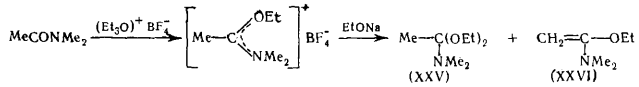


(XXI) (XXII) (XXIII) (XXIV)

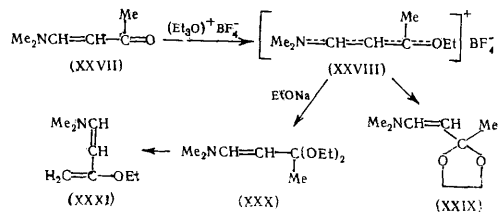
The reaction of trialkyloxonium fluoroborates with *NN*-disubstituted amides yields, after treatment of the intermediate fluoroborates with sodium ethoxide, the corresponding amide acetals: e.g. [20]



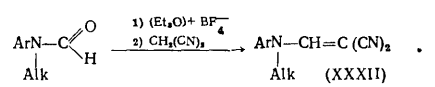
The alkylation of *NN*-dimethylacetamide with (II: R = C_2H_5) produces a fluoroborate salt, treatment of which with sodium ethoxide gives a mixture of the corresponding acetal (XXV) and the "*ON*-keten-acetal" 1-ethoxyvinyldimethylamine (XXVI)[20]:



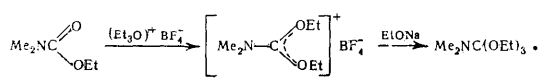
Alkylation of the vinylogue (XXVII) of *NN*-dimethylacetamide proceeds similarly. If the resulting fluoroborate (XXVIII) is decomposed with sodium glycollate, a stable cyclic acetal, *NN*-dimethyl-2-2'-methyldioxolan-2'-ylvinylamine (XXIX), is formed[20]. Reaction of (XXVIII) with sodium ethoxide gives an unstable diethyl acetal (XXX), vacuum distillation of which is accompanied by elimination of a molecule of alcohol with formation of the corresponding "keten-acetal" (XXXI)[20]:



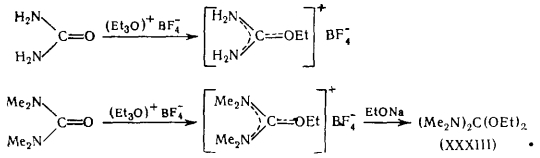
Amide acetals react very vigorously with various nucleophilic reagents[21]. It is not usually necessary to isolate the amide acetal (as in the preparation of amidines from amides—see above), and the intermediate fluoroborate salts can be used for further syntheses[25-27]. For example, *N''*-alkylanilinomethylenemalononitriles (XXXII) have been synthesised by the reaction of *N*-alkyl-*N*-arylformamides with trialkyloxonium fluoroborates followed by treatment with malononitrile in the presence of triethylamine[27]:



Urethanes and urea derivatives react similarly to amides with trialkyloxonium salts[4,20]. Thus triethyloxonium fluoroborate and ethyl *NN*-dimethylcarbamate give the corresponding salt, which is further converted by sodium ethoxide into orthocarbonic dimethylamide—a stable compound which is not hydrolysed under normal conditions[20]:

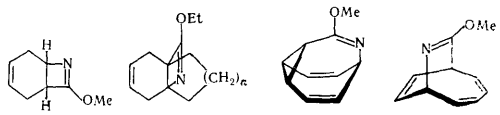


Similarly, the alkylation of urea[4] yields the fluoroborate of *O*-ethylisourea, and that of tetramethylurea the corresponding salt, from which diethoxy-*NNN'N'*-tetramethylmethylenediamine (XXXIII) was prepared by the action of sodium ethoxide[20]:

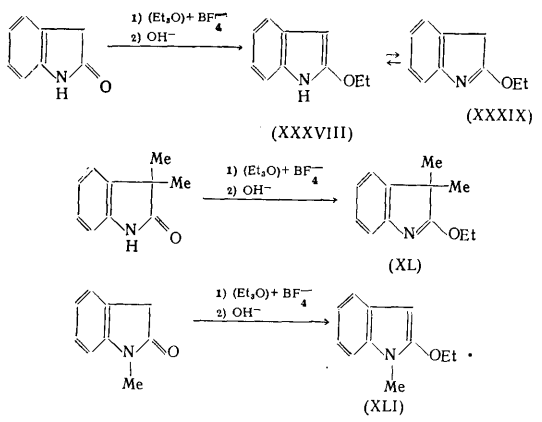


The reaction of trialkyloxonium fluoroborates with cyclic amides (lactams) has found wide application in organic synthesis. The resulting *O*-alkylated lactams have been starting materials for a large number of heterocycles, including members of novel heterocyclic systems[19].

The alkylation of simple lactams—2-oxopyrrolidine, 2-oxopiperidine, ϵ-caprolactam—by trialkyloxonium salts followed by treatment of the resulting fluoroborates with alkaline reagents gives high yields of the corresponding lactimidic esters[19,28,29]. This method has been used also to prepare lactimidic esters of phthalimidine[30], 1,2,3,4-tetrahydro-2-oxoquinoline[31,32], 3,5,7-trimethyl-2-oxoazepine[33], 2,3,4,5-tetrahydro-10-methyl-1-oxoazepino[3,4-*b*]indole[34], and also more complicated bi- and tri-cyclic lactams (XXXIV)–(XXXVII)[35-37].

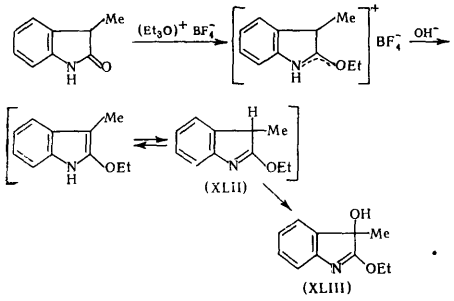


Interesting results have been obtained for the alkylation of oxindole and its derivatives with triethyloxonium fluoroborate[38-40]. Oxindole itself yields 2-ethoxyindole (XXXVIII), which on sublimation is converted into the lactimidic ester (XXXIX). The tautomeric equilibrium between (XXXVIII) and (XXXIX) in solution is demonstrated by comparing their infrared and proton magnetic resonance spectra with those of a model imine (XL) and a model enamine (XLI)[38]:



Comparison of the ionisation constants and also spectral data for the lactimidic esters of 3-substituted and 3,3-disubstituted 2-oxopiperidines (prepared from the corresponding lactams and triethyloxonium fluoroborate) indicate that such tautomerism is probably a general feature of lactimidic esters[41]. When 3-methyloxindole was alkylated with triethyloxonium fluoroborate, the product isolated was

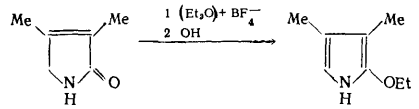
not the lactimidic ester (XLII) but (unlike what occurs with oxindole and 3,3-dimethyloxindole) an oxidation product, 2-ethoxy-3-hydroxy-3-methylindole (XLIII)[40]:



(XLII)

(XLIII)

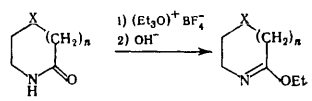
The alkylation of 3,4-dimethyl-2-oxopyrroline (XLIV) with triethyloxonium fluoroborate does not yield the corresponding lactimidic ester but a 2-ethoxypyrrole derivative (XLV):



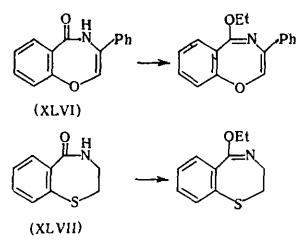
(XLIV) (XLV)

Migration of the double bonds probably occurs with formation of the stable aromatic ring[42].

Lactams containing a second heteroatom in the ring are alkylated selectively at the lactam carbonyl. Alkaline treatment of the products yields the corresponding lactimidic esters[18,32,43-48]:



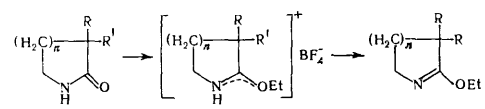
where $n = 1$, 2 and X = O, S, N.CO.CH$_3$. The corresponding lactimidic esters are obtained also from bicyclic lactams (XLVI) and (XLVII)[49,50]:



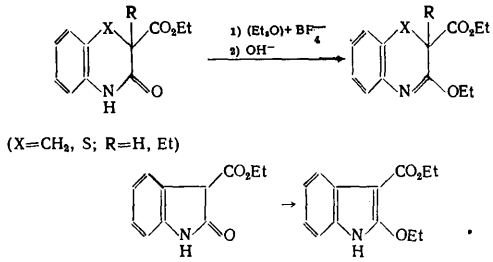
(XLVI)

(XLVII)

A considerable amount of work has been done on the alkylation of compounds containing other functional groups in addition to the lactam group[39,41,47,51-65]. In particular, the alkylation of a series of simple 3-mono- and 3,3-disubstituted lactams has been studied in connection with the synthesis of fused pyrimidine systems from lactimidic esters[41,51-56,58-62]:

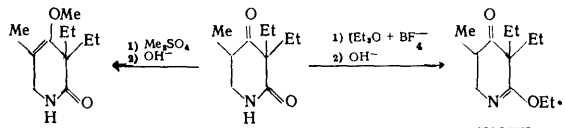


where with $n = 1$: R = COOC$_2$H$_5$ and R′ = H; with $n = 2$: R = H, C$_2$H$_5$, C$_6$H$_5$, Cl, Br, CH$_3$, OC$_2$H$_5$ and R′ = H, COOC$_2$H$_5$; and with $n = 3$: R = COOC$_2$H$_5$, CN and R′ = H. It was established that alkylation occurs selectively at the lactam carbonyl, the functional substituents remaining unaffected. The alkylation of benzo-derivatives of 3-ethoxycarbonyl-lactams proceeds similarly[39,47,63,66]:



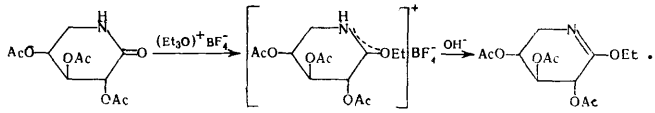
(X=CH$_2$, S; R=H, Et)

Alkylation of 3,3-diethyl-5-methyl-2,4-dioxopiperidine by triethyloxonium fluoroborate goes smoothly to the corresponding lactimidic ester (XLVIII)[51]. It is interesting that, with dimethyl sulphate as alkylating agent, the 4-carbonyl is alkylated with formation of the lactam (XLIX)[51]:

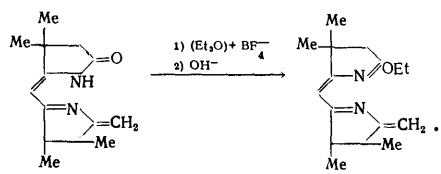


(XLIX) (XLVIII)

The mild conditions under which alkylation by tertiary oxonium salts takes place makes this method almost irreplaceable when the lactam ring contains such functional substituents as the acetoxy-group[57]:

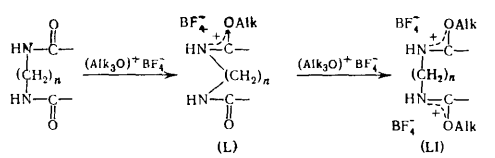


The great readiness of tertiary oxonium salts to alkylate a lactam carbonyl has been used for the preparation of intermediate products in the synthesis of corrin derivatives[64]:



Results have been published for the alkylation of compounds containing two amide functions. For example, triethyloxonium fluoroborate gives lower yields than usual of the lactimidic esters from 1-acetyl-3-oxopiperazine and its methyl 2-carboxylate[44,45,56], and also from ethyl 1-benzoyl-1,2,3,4-tetrahydro-3-oxoquinoxaline-2-carboxylate[47]. Together with the isolation of considerable quantities of the initial lactams, this can be explained by the simultaneous alkylation of the $N_{(4)}$-carbonyls.

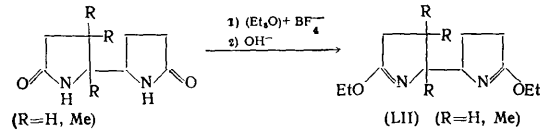
Examination of the scheme of alkylation of compounds containing two (or more) amide carbonyls reveals that, after the first amide group has been alkylated, attack by the alkylating agent on the second amide carbonyl is impeded by the electron-accepting action of the positively charged group in (L):



(L) (LI)

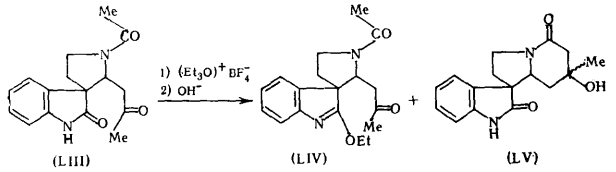
It is quite clear that this effect is weakened by large values of n, so that the decrease in electron density on the second amide carbonyl is insufficient to prevent formation of the dication (LI). As n becomes smaller, the electron density on this carbonyl decreases, and electrophilic attack by the alkylating agent will consequently be hindered.

The above principles can be illustrated by published results. Derivatives of 5,5'-dioxo-2,2'-bipyrrolidinyl react with triethyloxonium fluoroborate[6] to give high yields of bislactimidic esters (LII)[67,68]:



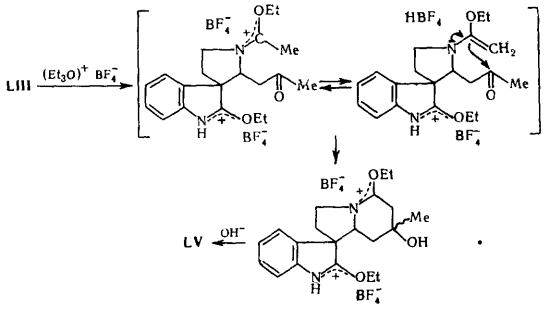
(R=H, Me) (LII) (R=H, Me)

Alkylation of the spiro-compound (LIII) with the same agent gave not only the corresponding lactimidic ester (LIV) but also a tetracyclic compound (LV)[69]:

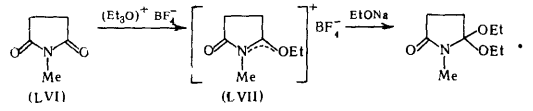


(LIII) (LIV) (LV)

Formation of the latter was regarded[70] as a consequence of alkylation of both amide groups:



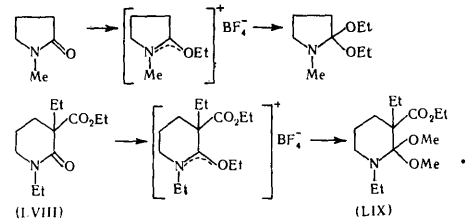
Nevertheless, only one carbonyl group is involved in the alkylation of N-methylsuccinimide (LVI) by triethyloxonium fluoroborate[71]:



(LVI) (LVII)

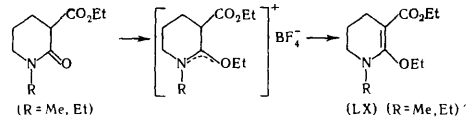
Indeed, it is difficult to imagine that under normal conditions the cation (LVII) could undergo further alkylation at the second carbonyl.

As in the alkylation of N-methylsuccinimide, the reaction of trialkyloxonium fluoroborates with N-substituted lactams yields lactam acetals after treatment with bases[2,20]. The examples of the N-methyl-2-oxo-derivatives of pyrrolidine, quinoline, benzoxazole, and benzothiazole show that this is probably a general method for the preparation of lactam acetals which are unsubstituted in position 3 of the ring[20]. The alkylation of a 3,3-disubstituted N-methyl-2-oxopiperidine (LVIII) also goes smoothly with formation of the corresponding acetal (LIX)[61]:

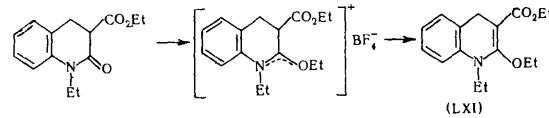


(LVIII) (LIX)

However, lactams containing a 3-ethoxycarbonyl group give enamines (LX) and (LXI)[59,63]—cyclic analogues of "*ON*-keten-acetals" (see beginning of this subsection)—as final products:

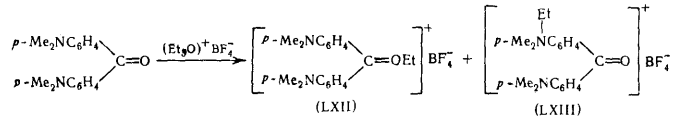


(R = Me, Et) (LX) (R = Me, Et)



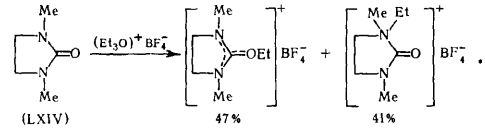
(LXI)

The results discussed above show that trialkyloxonium fluoroborates are excellent alkylating agents for the preparation of *O*-alkyl derivatives of amides, lactams, and related compounds, especially with respect to selectivity: when a lactam molecule contains several active groups, it is usually only the amide carbonyl that undergoes alkylation. However, examples are known in which alkylation by tertiary oxonium salts takes place ambiguously. Thus Michler's ketone yields not only the *O*-ethyl derivative (LXII) but also the isomeric N-alkyl compound (LXIII)[20]:



(LXII) (LXIII)

1,3-Dimethyl-2-oxoimidazolidine (LXIV) also gives a mixture of *O*- and N-alkylated products[20]:

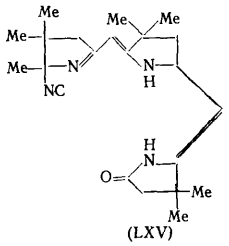


(LXIV)

It should be noted that triethyloxonium fluoroborate acts on the benzo-derivative of (LXIV) unambiguously with the formation of 2-ethoxy-1,3-dimethylbenzimidazolium fluoroborate[20].

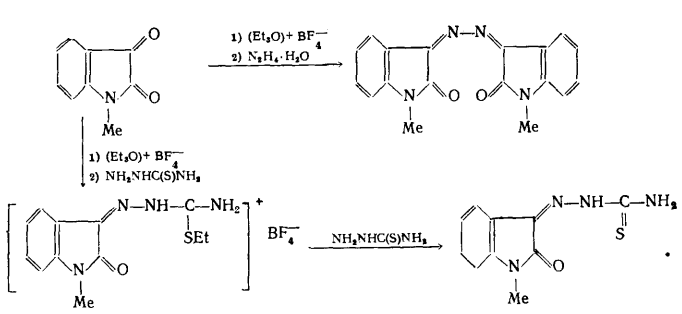
Until recently no cases were known of the N-alkylation of lactams by tertiary oxonium salts. However, it has

been reported recently that the reaction of the tricyclic lactam

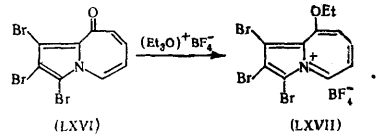


(LXV)

proceeds ambiguously to give a mixture of *N*- and *O*-isomers[72]. Treatment with hydrazine hydrate or thiosemicarbazide of the reaction mixture obtained from *N*-methylisatin and triethyloxonium fluoroborate yields the azine and the thiosemicarbazone of *N*-methylisatin[65]:



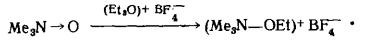
In concluding this subsection we must note a reaction which is closely related to the alkylation of lactams and their vinylogues—the action of triethyloxonium fluoroborate on the dicyclic oxoazepine (LXVI), resulting in the formation of an ethoxyazonia-azulene fluoroborate (LXVII)[73]:



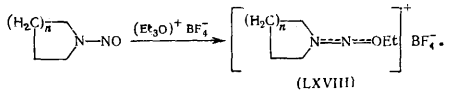
(LXVI) (LXVII)

3. Other *O*-Alkylations

Another reaction of tertiary oxonium salts is the *O*-alkylation of *N*-oxides[4] and *N*-nitroso-compounds[74]:

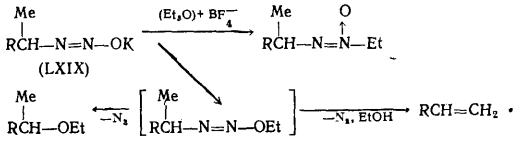


Investigation of the alkylation of *N*-nitrosoazacycloalkanes led to a new class of organic compounds—*O*-alkylnitrosoimmonium salts (LXVIII)[74]:



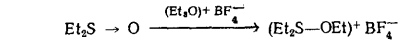
(LXVIII)

The alkylation of compounds containing nitrogen–oxygen bonds does not always occur unambiguously. Thus the reaction of triethyloxonium fluoroborate with diazoates (LXIX) yields not only *O*-alkylated products but also *N*-alkyl derivatives[75]:



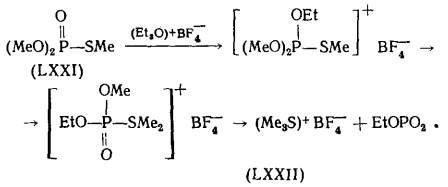
(LXIX)

As with *N*-oxides the alkylation of compounds containing an *S*-oxide group takes place at the oxygen atom with the formation of high yields of *S*-alkoxysulphonium salts (LXX)[4]:



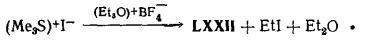
(LXX)

Interaction of the thioester (LXXI) with triethyloxonium fluoroborate gives trimethylsulphonium fluoroborate (LXXII). This process of alkylation was represented by the scheme[76]



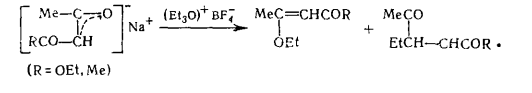
(LXXI) (LXXII)

The structure of the salt (LXXII) was proved[76] by its preparation from trimethylsulphonium iodide and triethyloxonium fluoroborate:



B. REACTIONS OF TRIALKYLOXONIUM FLUOROBORATES WITH AMBIDENT ANIONS

The molecules of ambident anions react with strongly electrophilic reagents mainly at the site of highest electron density[77,78]. This explains why the action of triethyloxonium fluoroborate on the sodium derivatives of acetoacetic ester‡ and penta-2,4-dione yields considerably greater proportions of *O*-alkylated products than when alkyl halides are used[79]. It is important to note that the reaction was conducted under heterogeneous conditions, which usually favour *C*-alkylation[80]:



(R = OEt, Me)

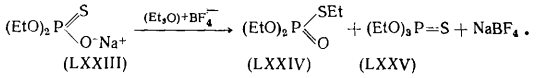
These results are consistent with the view that tertiary oxonium salts are considerably more strongly electrophilic than are alkyl halides.

Another study of the alkylation of metal derivatives of acetoacetic ester in hexamethylphosphoramide and in dimethyl sulphoxide has established that the use of triethyloxonium fluoroborate gives no higher yields of *O*-alkyl derivatives than are obtained with dialkyl sulphates, although the latter are considerably less electrophilic[81].

‡ The reaction of triethyloxonium fluoroborate with sodium acetoacetic ester had been accomplished earlier[1], but only the *C*-isomer had then been isolated (in 47% yield).

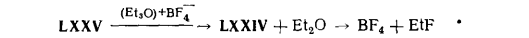
This anomaly was explained[81,82] on the assumption that the alkylating agent was not the tertiary salt but its reaction product with the solvent. This hypothesis is supported by the increased yields of *O*-ethyl derivatives obtained when the alkylation is conducted in a mixture of hexamethylphosphoramide and dichloromethane, and also by the ability of triethyloxonium fluoroborate to ethylate dimethyl sulphoxide[4].

Comparison of results for the alkylation of dialkyl phosphorothionate anions (LXXIII) by various alkylating agents, including triethyloxonium fluoroborate[83], also indicates the tendency of this reagent to attack at the site of highest electron density. Indeed, whereas the alkylation of (LXXIII) by alkyl halides and esters of mineral acids produces solely the *S*-derivatives (LXXIV), when the oxonium salt is used (LXXIV) is accompanied by the *O*-isomer (LXXV) in 8% yield:

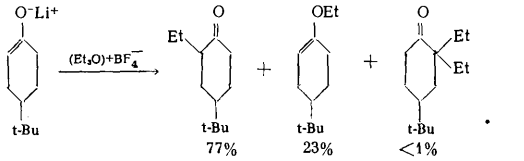


(LXXIII) (LXXIV) (LXXV)

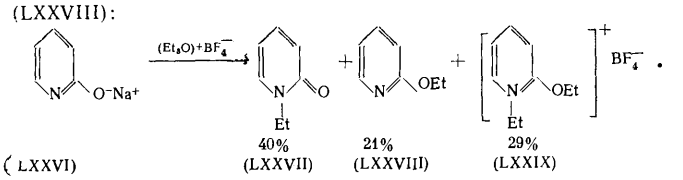
Since in the presence of triethyloxonium fluoroborate the *O*-isomer (LXXV) is partly converted into the *S*-isomer (LXXIV), the actual yield of the former may even be rather higher than the above value[83]:



Similarly, when triethyloxonium fluoroborate acts on the enolate anion [of 4-t-butylcyclohexanone], *C*-alkylation is accompanied by *O*-alkylation, whereas with methyl iodide as alkylating agent no *O*-alkylation products are found[84]:



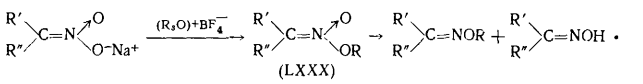
Results for treatment of the sodium salt of 2-hydroxypyridine (LXXVI) with triethyloxonium fluoroborate also support the principle that the more electrophilic alkylating agents show a greater tendency to *O*-alkylation. With alkyl halides this compound is alkylated at the nitrogen atom[85], the method being used most frequently for the preparation of 1-alkyl-1,2-dihydro-2-oxopyridine derivatives. On the other hand, when the tertiary oxonium salt is used, the *N*-ethyl derivative (LXXVII) is accompanied by a quite considerable quantity of 2-ethoxypyridine (LXXVIII)[85]. Another product is the *ON*-diethyl derivative (LXXIX), which results from further alkylation of the monoethylated compounds (LXXVII) and (LXXVIII):



(LXXVI) (LXXVII) (LXXVIII) (LXXIX)

The salt (LXXIX) also is an alkylating agent and capable of alkylating the initial compound (LXXVI)[85]. However, since it is less strongly electrophilic than triethyloxonium fluoroborate, it produces the *O*-ethyl derivative (LXXVIII) in considerably smaller yield (up to 9%), and the yield of the *N*-isomer (LXXVII) increases correspondingly (to 79%).

A fairly detailed investigation has been made of the alkylation of the sodium salts of nitroalkanes by trialkyloxonium fluoroborates[5,86,87]. The primary products are esters of the *aci*-nitro-derivatives (LXXX)[87], which are then converted into oximes and their ethers:

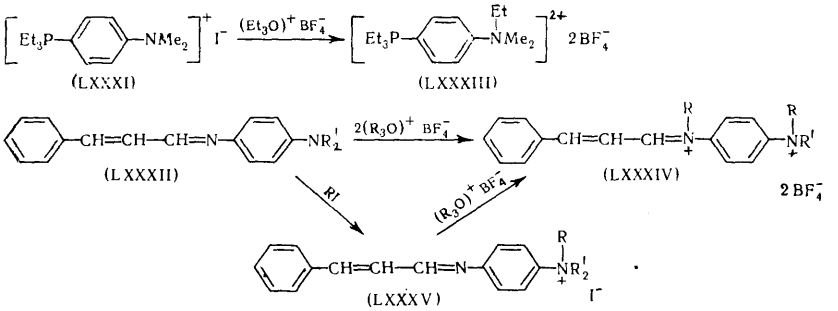


(LXXX)

It should be noted that triethyloxonium fluoroborate always gives higher yields than does the trimethyloxonium salt. Since alkylation is conducted in aqueous medium[4], this difference is probably due to the greater tendency of methyl derivatives to be hydrolysed.

C. *N*-, *P*-, AND *S*-ALKYLATION BY TRIALKYLOXONIUM FLUOROBORATES

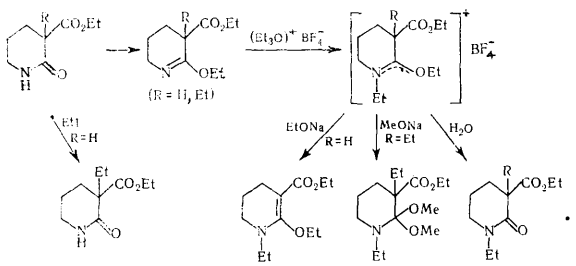
Oxonium salts have not found wide application for the alkylation of amines, since such strongly electrophilic reagents are not needed for this purpose. However, they can be usefully applied to the alkylation of compounds containing also strongly electron-accepting substituents, which weaken the nucleophilic character of the amino-group. Examples are provided by the alkylation of *p*-dimethylaminophenyltriethylphosphonium iodide (LXXXI)[88] and the cinnamylideneaniline derivative (LXXXII)[89], which yield the bivalent salts (LXXXIII) and (LXXXIV). The latter salt can be prepared in stages, in the first of which alkyl halides can be used to obtain the ammonium salt (LXXXV), but a trialkyloxonium fluoroborate is needed for the second stage[88]:



(LXXXI) (LXXXIII) (LXXXII) (LXXXIV) (LXXXV)

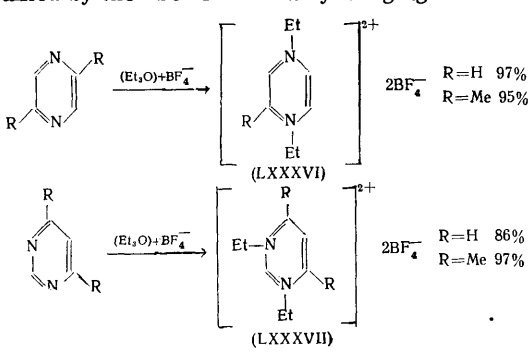
The strongly electrophilic character of trialkyloxonium salts enables several reactions to be accomplished that cannot be effected by other alkylating agents. Considerable interest therefore attaches to the use by Wittig et al. of trimethyloxonium fluoroborate for the quaternisation under mild conditions of sterically hindered amines such as e.g. *cis*- and *trans*-*N*-methyl-12-aza-1,2:3,4:7,8:9,10-tetrabenzocyclotrideca-1,3,5,7,9-pentaenes[90]. Furthermore, the reactions of a series of saturated heterocycles with tertiary oxonium salts reveal that not only axial but also equatorial isomers undergo alkylation, which is not observed with ethyl iodide[91].

Triethyloxonium fluoroborate has been successfully used to alkylate lactimidic esters of 2-oxopiperidines and 1,2,3,4-tetrahydro-2-oxoquinolines[59-61,63]. It is significant that this reaction takes place even when position 3 of the lactam ring is occupied by an electron-accepting substituent, and direct introduction of an *N*-alkyl group into the lactam cannot be achieved. Isolation of the intermediate fluoroborates then enables them to be used directly for preparing the corresponding α-alkoxy-enamines and acetals of the lactam[61]: e.g.

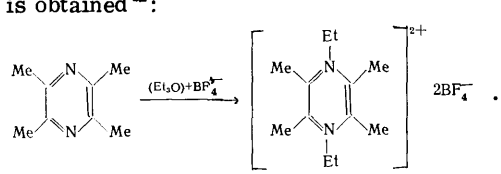


The above scheme shows that the use of tertiary oxonium salts makes possible the *N*-alkylation of compounds containing C=N double bonds.

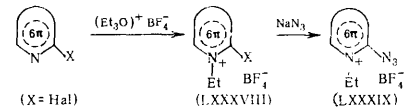
Heteroaromatic compounds similarly undergo smooth alkylation. Thus triethyloxonium fluoroborate acts on pyridine to give the *N*-ethylpyridinium salt[1], and pyrazine and pyrimidine derivatives yield the corresponding diquaternary salts (LXXXVI) and (LXXXVII), which cannot be obtained by the use of other alkylating agents[92]:



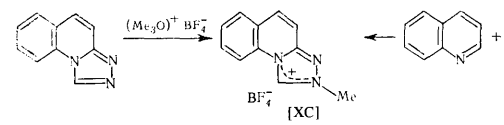
The yields of diquaternary salts decrease sharply when methyl groups are present in the $\alpha\alpha$-positions relative to the cyclic nitrogen atoms[92], and e.g. in the case of 2,3,5,6-tetramethylpyrazine only a 6% yield of the alkylation product is obtained[92]:



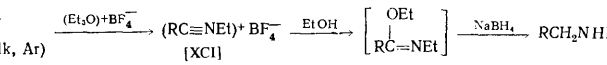
The alkylation of derivatives of thiazole, benzothiazole, naphtho[2,1-*d*]thiazole, benzoselenazole, benzimidazole, pyridine, isoquinoline, and 1,2,4-triazole also yields the corresponding fluoroborates (LXXXVIII), from which members of a new class of organic compounds—azidinium salts (LXXXIX)—have been prepared by reaction with sodium azide[93]:



Methylation of triazolo[4,3-*a*]quinoline with trimethyloxonium fluoroborate yields the corresponding fluoroborate (XC), whose structure has been proved by synthesis from quinoline and 2-ethoxy-1,1-dimethyldiazenium fluoroborate[94]:

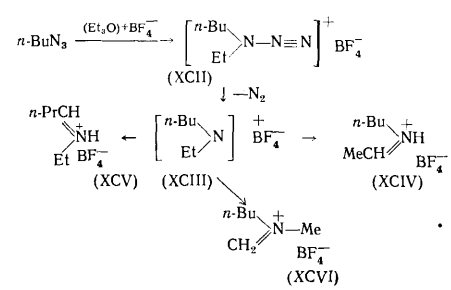


Trialkyloxonium fluoroborates act on nitriles to form nitrilium salts (XCI)[28,95,96], which on reduction with alcoholic sodium tetrahydroborate yield secondary amines[96]:



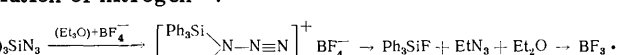
It should be noted that nitriles themselves are not reduced by alkali-metal tetrahydroborates.

Alkyl azides also undergo alkylation by triethyloxonium fluoroborate. With butyl azide, for example, the fluoroborate (XCII) is probably formed initially[97], and is then converted into a new salt (XCIII). The latter yields fluoroborates of Schiff bases (XCIV) and (XCV) together with an isomerisation product (XCVI):

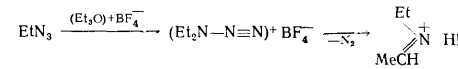


These compounds have not themselves been isolated, but their intermediate formation has been deduced from the presence of the corresponding amines and aldehydes after hydrolysis of the reaction mass[97].

The alkylation of triphenylsilyl azide proceeds rather differently, for the intermediate fluoroborate (which likewise was not isolated) undergoes cleavage without the evolution of nitrogen[98]:



If the reaction mixture contains excess of triethyloxonium fluoroborate, the ethyl azide undergoes further alkylation with the formation of ethylethylideneammonium fluoroborate[98]:



Tervalent phosphorus compounds react similarly to nitrogen-containing compounds, with the formation of quaternary phosphonium salts[88,99]:

$$PR_3 \xrightarrow{(Et_3O)^+BF_4^-} (EtPR_3)^+BF_4^-$$

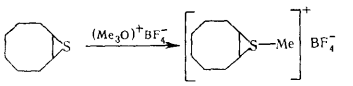
where R = OCH_3, OC_6H_5, $OCH_2CH_2C_6H_5$.

A considerable number of papers have been published on the *S*-alkylation of sulphur-containing compounds. Diethyl sulphide[4] and dimethyl disulphide[11] yield the corresponding sulphonium fluoroborates:

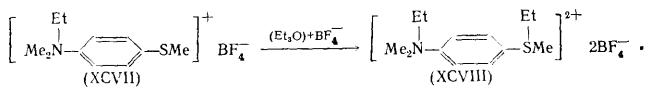
$$Et_2S \xrightarrow{(Et_3O)^+BF_4^-} (Et_3S)^+ BF_4^-$$

$$Me{-}S{-}S{-}Me \xrightarrow{(Me_3O)^+BF_4^-} (Me{-}S{-}SMe_2)^+ BF_4^-.$$

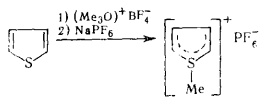
The alkylation of cyclo-octene sulphide occurs similarly[11]:



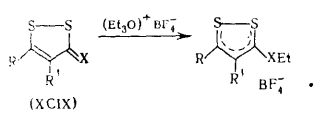
S-Alkylation takes place even when the sulphur atom is considerably depleted of electrons. Thus triethyloxonium fluoroborate acts smoothly on a *para*-substituted methyl phenyl sulphide (XCVII) containing in the ring such a strong electron acceptor as an ammonium group, with formation of a sulphonio-ammonium salt (XCVIII)[88]:



Even thiophen, in which the lone pair of the sulphur atom forms part of an aromatic sextet, has been alkylated[100]:

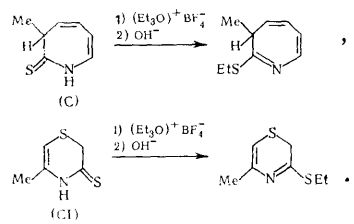


Thiocarbonyl compounds undergo alkylation by oxonium salts extremely readily. Thus the compounds (XCIX: X = S) give almost quantitative yields of the corresponding fluoroborates[101]:



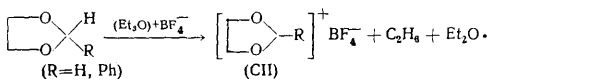
Appreciably lower yields of alkylation products are usually obtained when X = O[101].

Several examples have been described of the alkylation by triethyloxonium fluoroborate of thiolactams, e.g. thiocaprolactam[30], an azepinethione (C)[33], and a thiazinethione (CI)[102]. In all cases the final reaction products are the corresponding thiolactimidic esters:



D. TRIETHYLOXONIUM FLUOROBORATE AS ACCEPTOR OF THE HYDRIDE ION

Triethyloxonium fluoroborate can act not only as an alkylating agent but also as a hydride-ion acceptor[10,103,104]. It reacts with hydride-ion donors, e.g. dioxolan derivatives, to form carbonium ions (CII), ethane, and diethyl ether[10,103]:



It has also been reported[104] that triethyloxonium fluoroborate can act in this way with lithium tetrahydroaluminate and sodium tetrahydroborate.

The results surveyed in the present Review show that study of the chemistry of trialkyloxonium fluoroborates has proved extremely fruitful from both synthetic and theoretical points of view. The great reactivity of these salts, together with the relative simplicity of their preparation, makes them valuable starting materials for the synthesis of various organic compounds.

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The Chemistry of Ecdysones

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Ecdysones ara a group of structurally similar steroid compounds with hormonal activity in the moulting and metamorphosis of insects. The review deals with the sources from which ecdysones are isolated, their structure determination, and methods for their partial synthesis. The principal features of the biological activity of ecdysones and their synthetic analogues are also briefly outlined.
The bibliography includes 193 references.

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I. INTRODUCTION

A group of polyhydroxylated sterols with related chemical structures, isolated from arthropods and plants, is combined under the name of ecdysones (see the relevant reviews[1-9]). The group is of interest from both chemical (their unusual structure distinguishes them from all previously known steroid compounds) and biological standpoints, since ecdysones exhibit an extremely interesting physiological activity. The most common characteristic of the biological action of ecdysones is their capacity to cause the moulting and metamorphosis of insects. Depending on the source from which they are isolated (from plants or animals), these substances are divided into zooecdysones and phytoecdysones.

Zooecdysones are present in the organisms of various insects[10-13] and crustaceans[14-16], but their amounts are negligibly small. Thus 25 mg of α-ecdysone[17] was isolated from 500 kg of the pupae of the silkworm moth *Bombyx mori* and 9 mg of ecdysterone was obtained from two tons of the pupae[18,19]. The isolation of α-ecdysone corresponds to enrichment by a factor of 2×10^7 compared with its content in the initial biological material; the substance isolated in a pure form constitutes about 50% of the amount of hormones present in the initial material (according to biological assay). Only 2 mg of ecdysterone could be isolated from one ton of the crayfish *Jasus lalandei*[15]. Both the total content of zooecdysones and the relative amounts of the various components in their mixture depend on the insect species and the stage of development of the insect; for example, in some cases up to five individual active fractions were obtained[20].

The postembryonic development of insects is controlled by several hormones the interaction of which may be represented as follows[6]. Ecdysones (the moulting and metamorphosis hormones—MMH) are produced in the prothoracic gland of insects or in the analogous Y-organ of crustaceans. The secretion of ecdysones is controlled by the polypeptide ecdysiotropic hormone (ETH, also called the activating hormone), produced by the neurosecretory brain cells. Finally, the type of moulting induced by the MMH is determined by the Juvenile Hormone (JH), which is produced in the so called corpora allata). In the presence of the Juvenile Hormone larval moulting takes place and in its absence the metamorphosis of the larva to the pupa and of the pupa to the adult form (the imago). Ecdysones induce the moulting not only of insects but also of other classes of arthropods[21,22]. Probably steroids of this type already controlled the moulting of the common ancestors of anthropods in the Precambrian period (600 million years ago), i.e. ecdysones are the oldest steroid animal hormones. The MMH activity of ecdysones is determined in assays developed on various insects (see Karlson's review[23]). The most sensitive assay is on the housefly *Musca domestica*[24,25] and the simplest assay involves the rice pest *Chilo suppressalis*[26]. However, the commonest assay involves the blow-fly *Calliphora erythrocephala*[4,23,27]; the amount of ecdysones is sometimes expressed in "Calliphora units"—CE (1 CE $\simeq$ 0.01 μg of α-ecdysone, varying somewhat depending on the strain of the fly). One should bear in mind that the relative MMH activities of ecdysones found in various assays are different[28-30]. Biological control using assays of MMH activity proved particularly useful in the isolation of ecdysones from natural sources.

Ecdysones control physiological processes in insects associated with moulting and metamorphosis; their role in the formation of the puparium in the sclerotisation of the larval cuticle in the pupation process has been most thoroughly investigated. Ecdysones influence the carbohydrate, proteins, and nucleic acid metabolism[31-38]. The primary site of the action of ecdysones is the cell nucleus, more precisely its genetic material (see the relevant reviews[39-45]). Initially specific regulator genes are activated, then messenger RNA is synthesised, and finally proteins, in particular enzymes involved in the sclerotisation of the cuticle are synthesised. This mechanism of their action is satisfactorily consistent with the sequence of events in time. α-Ecdysone penetrates the cell nucleus 15–20 min after injection, causes the formation of chromosome "puffs" (i.e. gene activation) after 30–60 min, and increases the rate of synthesis of messenger RNA after 1–2 h, of microsomal RNA after 3–4 h, and of sclerotisition enzymes after 6–8 h.

The biosynthesis of zooecdysones in insects begins with cholesterol obtained from food (the insect organism is incapable of independent synthesis of steroids); the first step is dehydrogenation to 7-dehydrocholesterol[46-48]. Hydroxylation of the side chain apparently precedes the formation of the structural elements of the steroid skeleton; the C-25 and C-26 positions are hydroxylated faster than C-20.[49] α-Ecdysone is the precursor of ecdysterone in insects and crustaceans[50]. Zooecdysones are rapidly inactivated (cleaved) in insect tissues, the principal site

of their metabolism being the fat body [51-53]. The mechanism of the enzymatic cleavage of zooecdysones has not been established; it has only been shown that one of the first stages in the metabolism of ecdysterone may be the dissociation of their C-22–C-23 bond [54].

Numerous reports [55-63] on the isolation from plants of substances with MMH activity (phytoecdysones) appeared in 1966–1967. It has now been established that these substances are present in the fruit, leaves, bark, and roots of more than 100 plant species-mainly evergreen trees and ferns [64-67]; in higher fungi and algae compounds with MMH activity were not detected [56]. General methods have been developed for the extraction of total phytoecdysones from plants and for the chromatographic isolation of their individual components [68-70]. The content of phytoecdysones in plants depends on the species and the part of the plant; it usually exceeds by several powers of 10 the content of zooecdysones in crustaceans. For example, the amount of ecdysterone in the inflorescence of the saw-wort (*Serratula inermis*) can reach 2% of the dry weight [71].

The physiological role of phytoecdysones has not so far been elucidated. They may be the final products of the metabolism of sterols in plants or they can play a role in their growth and development (analogously to zooecdysones in insects). The hypothesis of the protective role of phytoecdysones in relation to insect plant pests [55,72] is apparently not confirmed by direct tests on their toxicity [73,74]. The biosynthesis of phytoecdysones in *Podocarpus* and *Taxus* species involves the usual sterol mechanism—via mevalonate and cholesterol, and their subsequent biochemical modification. The hydroxy-group at C-25 of the side chain is introduced after the hydroxy-groups at C-20 and C-22. [75-79]

Ecdysones exhibit physiological activity in relation to many groups of organisms. It has been reported that α-ecdysone accelerates plant growth [67,70] and induces the sexual cycle in protozoan symbionts of the insect *Cryptocercus* sp. [81] The effect of ecdysones on mammals is of special interest. In the first place both zooecdysones and phytoecdysones are fairly active anabolic agents (their activity is at the level of 4-chlorotestosteron) [82-87] and there are no toxic effects even after their prolonged administration [88]. The anabolic effect is probably associated with the mechanism of the action of ecdysones, which includes stimulation of protein synthesis; this is evidence that the transmission and counting processes in genetic information are common to insects and mammals. *In vitro* ecdysones inhibit the growth of sarcoma-180 cells and of embryonic fibroblasts [89,90], but they do not affect the growth of the Yoshida ascitic sarcoma [91]. α-Ecdysone shows virtually no hypocholesterolemic activity [92]. It should be remembered that human tissues do not exhibit MMH activity [93].

Three principal factors are of interest in the chemistry of ecdysones—the determination of their structures, their synthesis from other groups of steroids, and finally the relation between activity and structure and the preparation of structural analogues of ecdysones which maintain or enhance the type of physiological activity of practical importance to man.

II. THE STRUCTURE OF ECDYSONES

The study of the structure of ecdysones began in the 1950's with their isolation from insects in a crystalline state. The main obstacle in this work was the exceptionally low content of zooecdysones in biological material.

The structure of α-ecdysone was the first to be determined. X-Ray diffraction analysis and mass spectra made it possible to establish its empirical formula as $C_{27}H_{44}O_6$. [94] Dehydration of α-ecdysone (II) gave a low yield of the so called "Diels hydrocarbon" (I), which demonstrates the presence of the steroid skeleton in (II).

Table 1. Proton signals in the NMR spectrum of α-ecdysone (in C_5D_5N). [94]

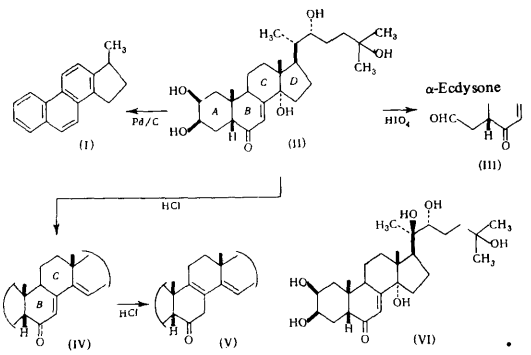
δ, p.p.m.	No. of protons	Functional groups
0.70	3	>C—CH_3 (angular methyl group)
1.05	3	>C—CH_3 (angular methyl group)
1.19	3	R>CH—CH_3 (doublet)
1.30		R>C(OH)—
1.38	6	R—$C(CH_3)_2$
1.92	21	CH and —CH_2—
4.18	1+2	HO— and HC<
5.75	4	HO
6.31	1	R—CO—CH=C(R)R
	44	

NMR spectroscopy proved to be particularly useful in the determination of the structure of α-ecdysone (Table 1) [94]—it made it possible to assign all 44 protons in the molecule to particular groups. The two angular methyl groups, the presence of which constitutes additional proof of the steroid structure of α-ecdysone, have the lowest chemical shifts. The third methyl group linked to a CH group, was assigned to the side chain (C-21). The two terminal methyl groups of the side chain were not found at a CH group as would be expected for a cholesterol derivative but at quaternary carbon atoms (six-proton singlet with δ = 1.38 p.p.m.). Hence it was concluded that, together with the two methyl groups, at C-25 there is also a hydroxy-group (if the methyl group were located at a double bond, the resonance signal would be observed at higher values of δ). This hydroxy-group gives rise to a hydroxyl proton signal at 4.18 p.p.m. In the NMR spectrum of α-ecdysone there is also a single signal corresponding to an olefinic proton (6.31 p.p.m.). It is suggested that this proton forms part of the structural element $RCOCH{=}CR_2$. The presence of a keto-group conjugated with a double bond in the α-ecdysone molecule is also confirmed by the ultraviolet ($\lambda_{max}^{CH_3OH}$ = 242 nm) and infrared (ν = 1657 cm^{-1}) spectra. The high degree of substitution of this group follows from the failure of its catalytic hydrogenation over palladium or platinum even under severe conditions [95]. The position of the $\alpha\beta$-unsaturated keto-groups in the ring system was established by comparing the spectra of a large number of model steroids [96] and by investigating their colour reactions [97]. These data led to the conclusion that the α-ecdysone molecule contains Δ^7-6-oxo-groups; this was confirmed in a study of the reactions of α-ecdysone under the influence of acids. When α-ecdysone is treated with HCl in

ethanol, a derivative with λ_{max} = 293 nm is formed initially and is then converted into a product with λ_{max} = 244 nm. These data were interpreted as indicating the initial dehydration of the readily eliminated tertiary 14-hydroxy-group with formation of a doubly unsaturated ketone (IV), which, as a result of the steric strain of the B ring, gradually isomerises to the unconjugated dienone (V).[95] These reactions also establish the position of the hydroxy-group at C-14; thus, of the six oxygen atoms in the α-ecdysone molecules, the positions of three were identified.

The ready cleavage of α-ecdysone by periodate to the corresponding dialdehyde (III)[95] demonstrates the presence in its molecule of a vicinal glycol group. The absence of volatile cleavage products in this oxidation indicates that the glycol group is in a steroid ring and not in a side chain. Biogenetic data suggest that one of the glycol hydroxy-groups is at C-3, as in all other natural steroids; then the second hydroxy-group can be at C-2 or C-4. The lack of similarity between model 3,4-diols and α-ecdysone[98] permits a choice in favour of a 2,3-diol. The position of the last hydroxy-group was established by studying the mass spectrum of α-ecdysone[94,95]. This yielded very intense peaks with m/e = 81 ($C_6H_9^+$) and m/e corresponding to $C_6H_{11}O^+$. Such fragments can be split off only from a side chain of the steroid molecule with dissociation of the C-20–C-22 bond, which establishes the location of the remaining hydroxy-group at C-22.

The final proof of the structure of α-ecdysone (II) was obtained by X-ray diffraction analysis, which confirmed all the conclusions arrived at above on the basis of chemical and spectroscopic data and in addition made it possible to establish the configuration of the hydroxy-groups in the steroid skeleton and in the side chain (2β-, 3β-, 14α-, 22R-) and the *cis*-junction of the A and B rings[99,100]:



Another representative of the group of ecdysones isolated from various natural sources[101,102] is ecdysterone (VI), which has one hydroxy-group more than α-ecdysone (II). Since according to the mass spectrum both hormones are identical up to C-19 and beyond C-22, this hydroxy-group can be located only at C-20. Comparison of the NMR spectra of ecdysterone and α-ecdysone leads to the same conclusion. The signals of the protons in the methyl groups at C-18 and C-21 in ecdysterone are displaced by 0.3–0.4 p.p.m. towards lower field compared with the analogous signals in the spectrum of α-ecdysone. Such changes are characteristic when a 20-hydroxy-group is introduced into a steroid molecule; this was confirmed by a comparative study of the NMR spectra of model compounds. The chemical properties and infrared and ultraviolet spectra of ecdysterone confirm the assignment of formula (VI).[103,104] On the basis of data for the interconversions of ecdysones in living organisms and the mode of their synthetic reactions, the 20*R*,22*R*-configuration of the hydroxy-groups in the side chain has been assigned to the majority of ecdysones, although it cannot be regarded as finally proved.

The structures of more than 30 zooecdysones and phytoecdysones have now been determined (Table 2). The elucidation of their structures is significantly aided by the knowledge of the structures of α-ecdysone (II) and ecdysterone (VI). Therefore in the determination of the structures of newly isolated ecdysones their structural similarity to (II) and (VI) is established on the basis of the infrared and ultraviolet spectra with the study of chemical reactions reduced to a minimum (usually only with HCl and HIO_4). The structural details are determined

Table 2. The structure of ecdysones.

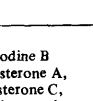
Name	Side chain of C-17 substituent and hydroxy-groups in steroid skeleton	Sources and references
19C Ecdysones Rubrosterone	 2β, 3β, 14α-(OH)$_3$	Plants (Refs.119-121) Synthesis*
27C-Ecdysones Ajugasterone C	 2β, 3β, 11α, 14α-(OH)$_4$	Plants (Ref.122)
Viticosterone E	 2β, 3β, 14α-(OH)$_3$	Plants (123)
2-Deoxyecdysterone	 3β, 14α-(OH)$_2$	Crustacea (Ref.124)
Inokosterone (viticosterone B)	 2β, 3β, 14α-(OH)$_3$	Insects (Ref.49) Plants (Ref.123, 125)
Callinecdysone A	(inokosterone isomer?)	Crustacea (Ref.16)
26-Hydroxyecdysterone	 2β, 3β, 14α-(OH)$_3$	Insects (Ref.126
Podecdysone B	 2β, 3β-(OH)$_2$ ($\Delta^{8(9),14}$-)	Plants (Ref.127
Polypodine B (ajugasterone A, viticosterone C, 5β-hydroxyecdysterone)	 2β, 3β, 5β, 14α-(OH)$_4$	Plants (Refs.123,128-130)
Ponasteroside A (warabisterone)	3β-D-glucoside of ponasterone A	Plants (Refs.131-133)
Ponasterone A	 2β, 3β, 14α-(OH)$_3$	Insects (Ref.49 Plants (Refs.107,110,126) Synthesis*

Table 2 contd.

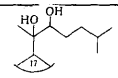
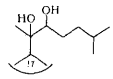
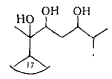
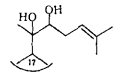
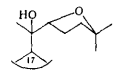
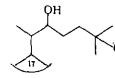
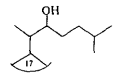
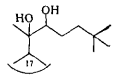
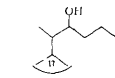
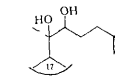
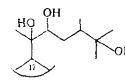
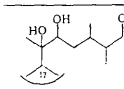
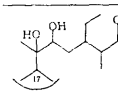
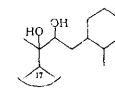
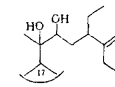
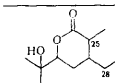
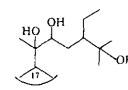
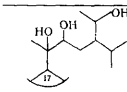
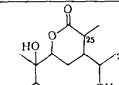
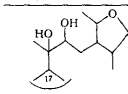
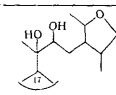
Name	Side chain of C-17 substituent and hydroxy-groups in steroid skeleton	Sources and references
Ponasterone B	 2α, 3α, 14α-$(OH)_3$	Plants (Refs.106, 107)
Ponasterone C	 2β, 3β, 5β, 14α-$(OH)_4$	Plants (Refs.106-108)
Pterosterone (viticosterone D)	 2β, 3β, 14α-$(OH)_3$	Plants (Ref.123,124)
Stachysterone C	 2β, 3β, 14α-$(OH)_3$	Plants (Ref.135)
Stachysterone D	 2β, 3β, 14α-$(OH)_3$	Plants (Ref.135)
Cheilanthone A	 2β, 3β, 14α-$(OH)_3$ (7,8-dihydro-)	Plants (Ref.136)
Cheilanthone B	 2β, 3β, 14α-$(OH)_3$ (7,8-dihydro)	Plants (Ref.136)
Shidasterone (isomer of ecdysterone)	 2β, 3β, 14β-$(OH)_3$	Plants (Ref.137)
α-Ecdysone	 2β, 3β, 14α-$(OH)_3$	Insects (Refs.14,17,138 Plants (Refs.62,72,139,140) Synthesis*
Ecdysterone (viticosterone A, isoinokosterone, crustecdysone, 20-hydroxyecdysone, polypodine A, β-ecdysone)	 2β, 3β, 14α-$(OH)_3$	Insects (Refs.14,18,103,141, 142) Crustacea (Ref.141, 143) Plants (Refs.55,57,60) Synthesis*
28C-Ecdysones Callinecdysone B	(isomer of Makisterone A?)	Crustacea (Ref.16)
Makisterone A (podecdysone D)	 2β, 3β, 14α-$(OH)_3$	Plants (Ref.127,144)
Makisterone B	 2β, 3β, 14α-$(OH)_3$	Plants (Ref.144,145)
29C-Ecdysones Amarasterone A	 2β, 3β, 14α-$(OH)_3$	Plants (Ref.146

Table 2 contd.

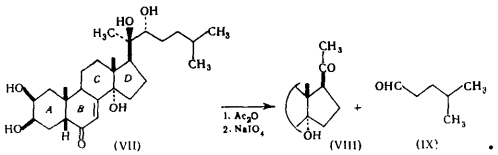
Name	Side chain of C-17 substituent and hydroxy-groups in steroid skeleton	Sources and references
Amarasterone B	 2β, 3β, 14α-$(OH)_3$	Plants (Ref.146)
Ajugasterone B	 2β, 3β, 14α-$(OH)_3$	Plants (Ref.147)
Capitasterone	 2β, 3β, 14α-$(OH)_3$	Plants (Ref.148)
Lemmasterone (makisterone C, podecdysone A)	 2β, 3β, 14α-$(OH)_3$	Plants (Refs.83,139,145,149)
Makisterone D	 2β, 3β, 14α-$(OH)_3$	Plants (Ref.145)
Precyasterone	 2β, 3β, 14α-$(OH)_3$	Plants (Ref.150)
Sengosterone	 2β, 3β, 5β, 14α-$(OH)_4$	Plants (Refs.115, 151)
Cyasterone	 2β, 3β, 14α-$(OH)_3$	Plants (Refs.113, 152)

*See Section III.

from the mass spectra, which yield information primarily about the structure of the side chain [105], and from NMR spectra, which in addition give information about the positions and configurations of the hydroxy-groups in the steroid skeleton†. A striking example is provided by the determination of the structure of the phytoecdysone ponasterone A. [107,109,110]. Apart from the corresponding

†It should be noted that such neglect of chemical methods for structural determinations can lead to significant errors. For example, a 2α,3α-configuration of the hydroxy-groups in the A ring of ponasterone C was assigned on the basis of spectroscopic studies [106,107]. A more careful reinvestigation [108] made it necessary to invert this configuration to 2β,3β- and moreover led to the detection in the ponasterone C molecule of an additional 5β-hydroxy-group, the presence of which had been overlooked as a result of the incorrect interpretation of the mass spectrum.

biological activity, its classification as an ecdysone is demonstrated also by ultraviolet and infrared spectra, which are similar to those of ecdysterone. Ponasterone A ($C_{27}H_{44}O_6$) has six oxygen-containing groups, one of which is part of the $\alpha\beta$-unsaturated ketone group (ultraviolet and infrared spectra and NMR signal of the olefinic proton at 6.17 p.p.m.). The formation of a diacetamide indicates the presence of four hydroxy groups in two vicinal diol groups; this is also confirmed by oxidation with $NaIO_4$, which involves the consumption of two moles of the oxidant. The location of the fifth hydroxy-group at C-14 follows (by analogy with α-ecdysone) from the successive formation of compounds with λ_{max} = 294 and 241 nm when ponasterone A is treated with HCl and its 14α-configuration follows from a comparison of the chemical shifts of the protons in the methyl groups at C-18 and C-19 in the NMR spectra of ponasterone A and ecdysterone. Ponasterone A readily forms a triacetate; the NMR spectrum of the latter ($CDCl_3$) has signals at 4.82, 5.05, and 5.32 p.p.m., which can be attributed to three carbonyl protons at C-22, C-2, and C-3. Therefore three hydroxy-groups are secondary and the remaining two are tertiary. Moreover, in the NMR spectrum of ponasterone A there is a doublet at 0.82 p.p.m. corresponding to the methyl groups at C-26 and C-27, which demonstrates the absence of a hydroxy-group at C-25 (in the spectra of α-ecdysone and ecdysterone these signals are at 1.38 and 1.34 p.p.m. respectively). Comparison of the signals due to the protons at C-18, C-19, and C-21 (at 1.16, 1.03, and 1.51 p.p.m. in ponasterone A and at 1.19, 1.06, and 1.55 p.p.m. in ecdysterone) leads to the conclusion that the corresponding methyl groups have the same environment and to the assignment of formula (VII) to ponasterone A. The formula is confirmed by the results of the oxidation of ponasterone A 2-monoacetate by $NaIO_4$ which results in the formation of the 20-ketone (VIII).[107] The identity of this ketone with the product of the analogous oxidation of ecdysterone and the intermediate in the partial synthesis of α-ecdysone [111,112] demonstrates unambiguously that the tetracyclic structures of all three ecdysones are the same up to C-21. The structure of the side chain of ponasterone A is confirmed by the isolation of isohexanal (IX) in oxidation with $NaIO_4$ and also by the presence in the mass spectrum of an intense peak with m/e = 83 corresponding to the $C_6H_{11}^+$ fragment formed on dissociation of the C-20–C-22 bond [107]. It should be noted that the structures of α-ecdysone, ecdysterone, ponasterone A, and also rubrosterone have been demonstrated by their synthesis (see section III).



(VII) (VIII) (IX)

Other physicochemical research methods have proved very helpful in the determination of the structure of ecdysones. The optical rotatary dispersion (ORD) curves are used mainly to determine the type of junction between A and B rings. The Δ^7-6-oxo-group of ecdysones exhibits a Cotton effect at about 240 nm ($\pi \rightarrow \pi^*$ transition) and at about 340 nm ($n \rightarrow \pi^*$ transition). In both cases the amplitude for the *trans*-A/B isomers is much higher than for the *cis*-A/B isomers [102,106,107,109,113]. Apart from the amplitudes, there is a significant difference (by 8–10 nm) between the positions of the peaks in the ORD curves for the *cis*- and *trans*-isomers. Thus in the region of the $n \rightarrow \pi^*$ transition natural α-ecdysone has peaks at 377 and 361 nm, while its *trans*-A/B isomer has peaks at 366 and 351 nm.[114]

The circular dichroism (CD) curves also show a shift of the maximum by 7–8 nm towards longer wavelengths on passing from the *trans*- to the *cis*-A/B junction[114]. A similar shift is observed when a 5β-H atom in the ecdysone molecule is replaced by a 5β-hydroxy-group, which makes it possible to determine the position of the latter [108,115]. The CD curves for the α-glycol dibenzoates of the ecdysone series have been used to determine their chirality in the elucidation of the structures of ponasterones A–C, polypodine B, and ajugasterone [108,116,117]. The use of the fluorescence spectra of ecdysterone and inokosterone for the analysis of a mixture of these compounds, which occur together in many plants, is also noteworthy [118].

The names and formulae of the ecdysones known at the present time are given in Table 2. According to the number of carbon atoms in the molecule they can be divided into four groups 19C-, 27C-, 28C-, and 29C-ecdysones. Phytoecdysones belonging to all four groups have been found, but zooecdysones occur only in the second group (with the sole exception of callinecdysone B, which apparently has 28 carbon atoms). The majority of ecdysones have the same characteristic set of substituents in the steroid skeleton: 2β, 3β, 14α-hydroxy-groups, a Δ^7-6-oxo-group, and a *cis*-A/B junction. The side chain always contains (except in rubrosterone which has no side chain) a hydroxy-group at C-22 and frequently at C-20; in certain cases oxygen-containing substituents occur at C-24, C-25, C-26, C-28, or C-29 carbon atoms of the side chain. Thus not only the MMH activity but also the common features of the chemical structures of the known ecdysones justify their classification as a special group of natural compounds.

The deviations from the above typical structure are comparatively small. Polypodine B, ponasterone C, and sengosterone have an additional 5β-hydroxy-group and ajugasterone C an 11α-hydroxy-group. The 2α,3α-configuration of the hydroxy-groups in the A-ring of ponasterone B has been demonstrated, instead of the 2β, 3β-configuration characteristic of the remaining ecdysones, and shidasterone apparently has a 14β- and not a 14α-hydroxy-group. In cheilanthones A and B there is no Δ^7-linkage and podecdysone B has a $\Delta^{8(9),14}$-diene system, which may be formed during its isolation as a result of the scission of the 14α-group.

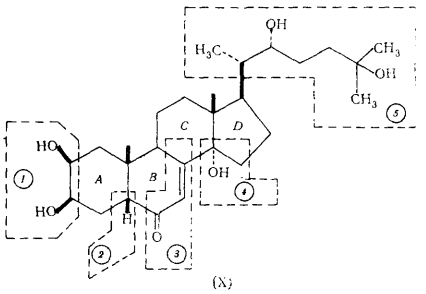
In natural sources so far only two ecdysone derivatives substituted at a hydroxy-group have been found—viticosterone E (ecdysterone 25-acetate) and ponasteroside A (ponasterone A 3β-glyucoside).

III. SYNTHESIS OF ECDYSONES

The synthesis of ecdysones, which was achieved almost immediately after the determination of their structure, is evidence of a high level of development and considerable

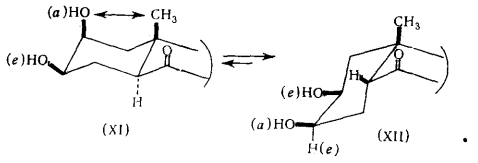
advances in steroid chemistry. Several groups of investigators have now developed four schemes for the partial synthesis of ecdysones (X). Unfortunately none of the investigators quote the yields in all the stages, which precludes an exact quantitative comparison of the effectiveness of these schemes.

In the ecdysone (X) molecule it is possible to isolate five principal structural elements, which distinguish this group of natural compounds from other steroids. These are the vicinal 2β,3β-diol group in the A ring (1), the 5β-hydrogen atom between the A and B rings (2), the Δ^7-6-oxo-group in the B ring (3), the 14α-hydroxy-group between the C and D rings (4), and finally the side chain in the 17β-position of the D ring (5).



(X)

These structural elements are introduced by various methods depending on the structure of the initial compound. For example, the 2β,3β-diol group is introduced into Δ^2-compounds by the *cis*-hydroxylation of the double bond and into 3-oxo-5α-steroids either by bromination in the 2α-position with subsequent replacement of bromine by a 2β-acetoxy-group (with silver acetate) or by auto-oxidation in an alkaline medium and subsequent reduction of the resulting 2,3-diketone with $NaBH_4$.[153] The Δ^7-bond is as rule introduced on bromination–dehydrobromination of 6-oxosteroids, but the Δ^7-6-oxo-group can be formed also directly by the oxidation of $\Delta^{5,7}$-steroids[154,155]. The 14α-hydroxy-group is likewise introduced into the molecule by several methods. The most common is the allylic oxidation of Δ^7-6-oxosteroids with SeO_2.[156] The pathway via the formation of enol acetates of these compounds with subsequent oxidation by peracids is also used[157]. Finally, microbiological hydroxylation[158] and photochemical oxidation of $\Delta^{8(14)}$-6-oxosteroids for this purpose have been described[159,160]. The reaction of steroid 20-ketones or 22-aldehydes with lithium or magnesium derivatives of the corresponding acetylene alcohols containing all the necessary substituents serves as the usual method for the introduction of the side chain. The problem of ensuring the 5β-configuration, i.e. the *cis*-junction of the A and B rings merits special attention. In the usual 6-oxosteroids the 5α-isomer is much more stable than the 5β-isomer[161]. However, in 2β,3β-dihydroxy-6-oxosteroids, specific examples of which are ecdysones, the *meta*-diaxial interaction between the 2β-hydroxy-group and the methyl at C-19 in the 5α-isomer (XI) lowers its stability compared with the 5β-isomer (XII), where such interaction is absent. Therefore the 5β-isomer predominates in the equilibrium mixture [the ratio 5β : 5α = (2 – 4) : 1, depending on the structure of the steroid]; this fact is used in the synthesis of ecdysones from 5α-steroids.



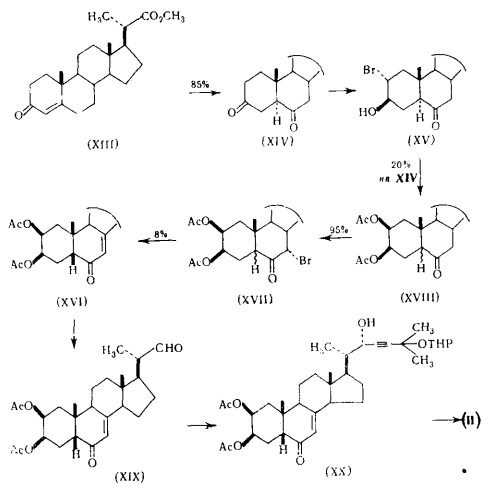
(XI) (XII)

The schemes for the synthesis of ecdysones which have not been developed differ not only in the types of reactions used to introduce various structural elements but also in the order of their introduction. In considering them particular attention must be paid to the syntheses of α-ecdysone, since these were in fact used to develop the main synthetic procedures. The syntheses of ecdysterone usually differ only in the methods of introduction of the side chain and the syntheses of rubrosterone, a metabolite of active ecdysone, are not usually of independent importance‡. In addition plants constitute a rich source of the last two ecdysones, whereas the requirements for α-ecdysone are mainly satisfied by the synthetic product.

In 1966 a group of Swiss chemists described a partial synthesis of α-ecdysone (II) in which the structural elements [see formula (X)] were introduced according to the scheme *1* → *3* → *2* → *4* → *5*.[163–167] The initial compound in this synthesis is the methyl ester of bisnorcholenoic acid (XIII) obtained from ergosterol or stigmasterol. The formation of ethyleneketal, the epoxidation of the Δ^5-bond with peracetic acid to a mixture of 5ξ,6ξ-epoxides, and the isomerisation of this mixture under the influence of perchloric acid led to the 3,6-diketone (XIV). The bromination and selective reduction of the 3-oxo-group with $LiAl(t\text{-}C_4H_9O)_3H$ yielded the 2α-bromo-3β-hydroxy-compound (XV), the acetylation of which and the replacement of bromine by an acetoxy-group led to a mixture of the 2β,3β-diacetates (XVIII) epimeric at C-5. The Δ^7-bond was introduced by bromination under acid conditions; the mixture of 5- and 7-bromoketones formed initially isomerises to the 7α-bromo-derivative (XVII). The elimination of HBr from the latter yields the Δ^7-6-oxo-compound, which is also a mixture of isomers at C-5. Alkaline isomerisation at the C-5 centre is accompanied in this case by epimerisation also at the C-20 centre and the shifte of the Δ^7-bond to the $\Delta^{8(14)}$-position; therefore halogenolysis (LiI in boiling lutidine) was employed to obtain the 5β-isomer (XVI). The 22-methoxycarbonyl group of compound (XVI) was reduced to the corresponding aldehyde (XIX) by allowing $LiAl(t\text{-}C_4H_9O)_3H$ to react with the carbonyldi-imidazole derivative. The side chain was introduced by a Grignard reaction with the MgBr derivative of the tetrahydropyranyl (THP; C_4H_9O) ether of 2-methylbut-3-yn-2-ol. This reaction yielded a mixture of the required 22*R*-isomer (XX) and the corresponding 22*S*-derivatives, which were separated by chromatography on silica and were treated separately. Catalytic hydrogenation of the triple bond in the side chain, the introduction of the 14α-group by the action of SeO_2 in dioxan, and acid hydrolysis of the

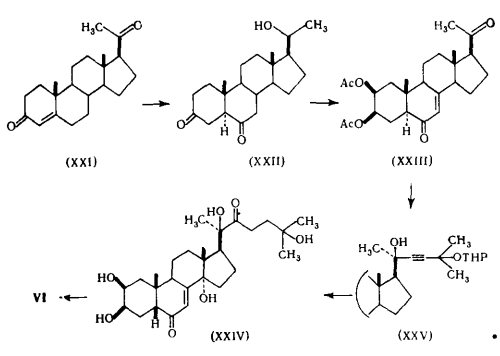
‡A novel synthesis of rubrosterone via *i*-steroids was developed recently[162], but it has not been extended to active ecdysones.

protecting groups (acetate, THP ether) yielded α-ecdysone (II). Analogous treatment of the 22*S*-epimer (XX) made it possible to obtain 22-iso-α-ecdysone. Rubrosterone was synthesised according to the same scheme [168].



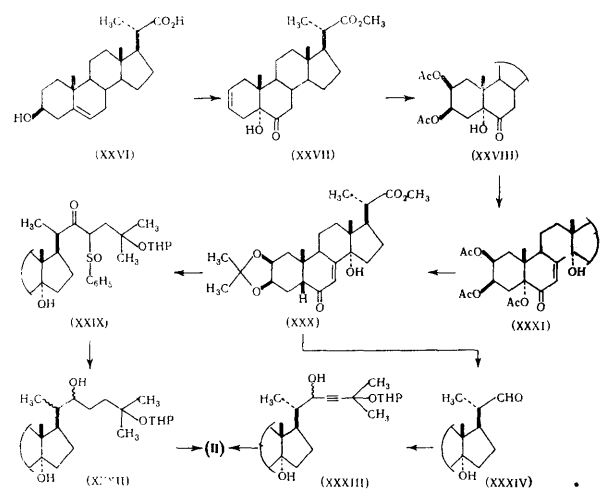
The chief disadvantage of the above method of synthesis is a low yield in the (XVII) → (XVI) isomerisation stage. Therefore in the synthesis of ecdysterone by the same group of investigators the formation of the 5β-configuration was transferred to the end of the synthesis and was combined with the alkaline hydrolysis of the protecting groups.

Ecdysterone (VI) was synthesised according to the following scheme [169]. The 3,6-diketone (XXII) obtained in four stages from progesterone (XXI) as in the synthesis of α-ecdysone [the (XIV) → (XV) → (XVIII) → (XVII) → (XVI) transition], was converted in seven stages into the intermediate (XXIII) containing the 2β,3β-diol and Δ⁷-6-oxo-groups. The side chain was introduced into this compound by the reaction with the MgBr derivative of the THP ether of 2-methylpent-4-yn-2-ol.



This yielded a 4 : 1 mixture of the 20*R*-isomer (XXV) and the 20*S*-isomer. The oxygen-containing substituent at C-22 was introduced by the catalytic hydration of the triple bond in the side chain [in the presence of $Hg(OAc)_2$]. The subsequent introduction of the 14α-hydroxy-group by oxidation with SeO_2 and alkaline hydrolysis of the protecting groups, accompanied by inversion at C-5 led to compounds (XXIV), which differs from ecdysterone (VI) only by the presence of an oxo-group at C-22. The reduction of this oxo-group with $LiAl(t\text{-}C_4H_9O)_3H$ led to a mixture of natural ecdysterone (VI) and its 22-isomer, which were separated chromatographically. Direct catalytic hydrogenation of compound (XXV) with subsequent treatment according to the above scheme made it possible to obtain 22-deoxy-ecdysterone, which is used in the study of the biosynthesis of ecdysterone [170,171].

Another synthesis of α-ecdysone and ecdysterone according to the *1* → *3* → *4* → *2* → *5* scheme was proposed in 1966 by a group of chemists in the USA. [172-175] The synthesis began with a derivative of bisnorcholenoic acid (XXVI), which was converted by acetylation and treatment with diazomethane into the 3-acetate of the methyl ester. Hydroxylation of the latter and the Δ^5-bond, hydrolysis of the 3-acetoxy-group, oxidation at C-6 with *N*-bromosuccinimide, tosylation, and the elimination of TsOH by treatment with Li_2CO_3 led to compound (XXVII) with an overall yield up to 50% with respect to the initial acid (XXVI). *Cis*-hydroxylation of the Δ^2-bond with silver acetate and molecular iodine in acetic acid and subsequent acetylation gave compound (XXVIII), in which a Δ^7-bond was introduced by bromination in an acid medium and subsequent elimination of HBr by treatment with Li_2CO_3. The acid-catalysed acetylation of the tertiary 5α-hydroxy-group and the introduction of the 14α-hydroxy-group by allylic oxidation with SeO_2 yielded compound (XXXI), which already contains three fragments of the α-ecdysone structure. The introduction of the next fragment (a 5β-hydrogen atom) was achieved in four stages. The 5α-acetoxy-group was removed by reduction with $CrCl_2$; next the alkaline hydrolysis of the 2,3-diacetate was carried out, the diol group was protected by the formation of an acetonide, and finally isomerisation at C-5 by heating with an aqueous-methanolic solution of potassium carbonate gave a 1 : 3 mixture of the 5α- and 5β-isomers. The pure 5β-isomer (XXX) was isolated from this mixture by chromatography on silica.

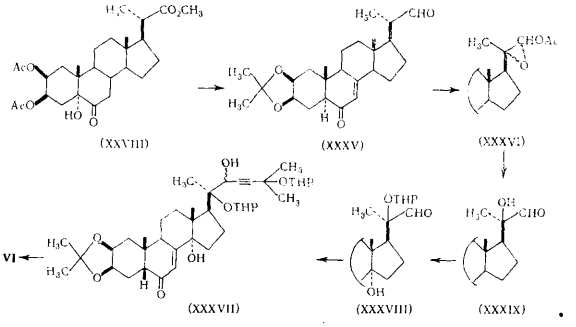


The introduction of the side chain characteristic of α-ecdysone into compound (XXX) was achieved by two methods. In the first version [173] the 6-oxo-group was reduced with $LiAl(t\text{-}C_4H_9O)_3H$ to a mixture of 6α- and 6β-hydroxy-derivatives; its alkylation at C-22 with the

lithium salt of the THP ether of 2-methyl-4-sulphoxyphenylbutan-2-ol by the method of Corey and Chaykowsky[176] led to compound (XXIX). Hydrogenolysis of the sulphoxyphenyl group of this compound with aluminium amalgam and reduction of the 22-oxo-group with $LiAlH_4$ (the 6-oxo-group is reduced at the same time) gave the 22-hydroxy-derivative (XXXII), which is a mixture of epimers at C-20 and C-22. Resynthesis of the 6-oxo-group by oxidising this mixture with MnO_2 (only the allylic 6ξ-hydroxy-group is affected) and hydrolysis of the protecting groups with dilute HCl led to a mixture of the corresponding isomers of α-ecdysone, from which the natural hormone (II) was isolated in 12% yield with respect to compound (XXX) by chromatography on silica.

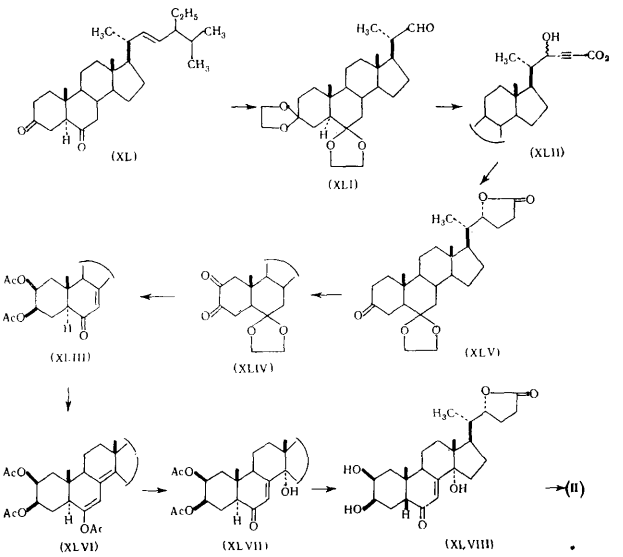
The inadequate stereospecificity of this synthesis made necessary a modification in which the introduction of the side chain into compound (XXX) does not involve isomerisation at the C-20 centre[11]. The methyl ester (XXX) was converted into the aldehyde (XXXIV) by a fairly complex procedure. Reduction of the 6-oxo-group with $LiAl(t\text{-}C_4H_9O)_3H$, reduction of the 22-carboxymethyl group with $LiAlH_4$, and resynthesis of the 6-ketone by oxidation with MnO_2 made it possible to obtain from (XXX) the corresponding 22-hydroxy-derivative. Its oxidation to the aldehyde (XXXIV) was achieved by treatment with dicyclohexylcarbodi-imide in dimethyl sulphoxide in the presence of trifluoroacetic acid as a catalyst[177]. The reaction of the aldehyde (XXXIV) with the lithium derivative of the THP ether of 2-methylbut-3-yn-2-ol gave a mixture of 22-hydroxy-compounds (XXXIII) epimeric at C-22. Its separation by preparative thin-layer chromatography on silica, catalytic hydrogenation of the triple bond, and hydrolysis of the protecting groups yielded α-ecdysone (II) and 22-iso-α-ecdysone.

The synthesis of ecdysterone (VI) was achieved by a similar scheme[178,179]. The starting material in this synthesis is compound (XXVIII), already described, which was converted in eight stages into the 22-aldehyde (XXXV) [similarly to the conversion (XXVIII) → (XXXI) → (XXX) → → (XXXIV) in the synthesis of α-ecdysone by the method of the same group of investigators]. Acetylation of the enol of the aldehyde (XXXV) and oxidation of the resulting enol acetate with *m*-chloroperbenzoic acid gave a mixture of isomers of the 20ξ,22ξ-epoxide (XXXVI). Its hydrolysis with $KHCO_3$ in aqueous methanol yielded the 20*R*-hydroxy-22-aldehyde (XXXIX) and its 20*S*-isomer in proportions of 5 : 3; the isomers could be separated by chromatography on silica. Protection of the 20-hydroxy-group by the THP ether and the introduction of the 14α-hydroxy-group by oxidation with SeO_2 led to compound (XXXVIII), which was used directly to introduce the side chain. Reaction with the MgCl derivative of the THP ether of 2-methylbut-3-yn-2-ol and its isomerisation at C-5 (K_2CO_3–H_2O–CH_3OH) led to compound (XXXVII) (in $5\alpha : 5\beta = 1 : 3$ equilibrium mixture). Finally, catalytic hydrogenation of the triple bond in the side chain (5% Pd/C)§ and hydrolysis of the protecting groups with dilute HCl gave ecdysterone (VI). An advantage of this method of synthesis of ecdysones is the use of the convenient procedure for the introduction of the 2β,3β-diol group by the *cis*-hydroxylation of the Δ^2-bond; the disadvantages include primarily the unsatisfactory choice of bisnorcholanoic acids as starting materials (in view of the laborious nature of the method of their conversion into the 22-aldehydes selected by the authors).



(XXVIII) (XXXV) (XXXVI) (XXXVII) (XXXVIII) (XXXIX)

The third method of synthesis of ecdysones according to the scheme *5a* → *1* → *3* → *4* → *2* → *5b* (the side chain is built up in two stages) was published in 1967–1968 by a group of Japanese chemists. The starting material for the synthesis of α-ecdysone[181] was the 3,6-diketone (XL) obtained from stigmasterol and converted by ketalisation, ozonolysis, and the reduction of the ozonide with zinc dust in acetic acid into the diketal of the 22-aldehyde (XLI). Partial synthesis of the side chain was achieved through the introduction of the ethynyl group by reaction with BrMgC≡CH and subsequent reaction of the MgBr derivative of the resulting ethynylmethanol with carbon dioxide. Catalytic hydrogenation and acid hydrolysis of the acetylenic hydroxyacid (XLII) gave a mixture of 3,6-diketones epimeric at C-22, in which the required 22*R*-isomer predominated. Selective reduction of the 3-oxo-group with $NaBH_4$, ketalisation of the 6-oxo-group, and oxidation of the 3-hydroxy-group to the 3-ketone by the CrO_3 complex of pyridine resulted in the 6-monoketal (XLV) required for further synthesis. Auto-oxidation of this compound in the presence of $t\text{-}C_4H_9OK$ gave an oily mixture of the two possible enolic forms of the 2,3-diketone (XLIV). Reduction of this mixture with $NaBH_4$ and subsequent chromatographic separation made it possible to isolate the 2β,3β-diol, which was converted into the corresponding diacetate.



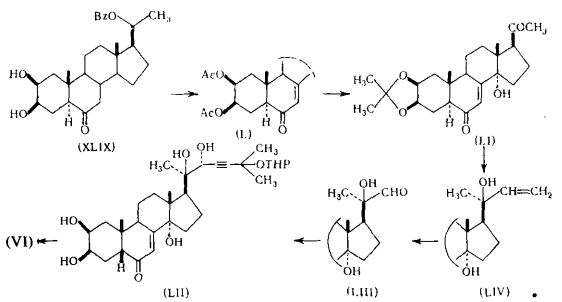
(XL) (XLI) (XLII) (XLIII) (XLIV) (XLV) (XLVI) (XLVII) (XLVIII) (II)

§The hydrogenation is also accompanied by the hydrogenolysis of the 25-hydroxy-group and the 25 deoxy-derivative of ecdysterone (ponasterone A) is formed as a side product[180].

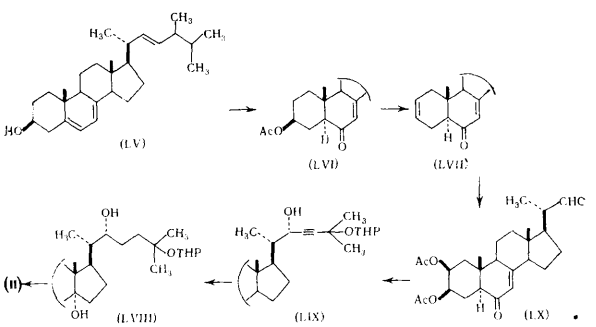
Bromination at C-7 with subsequent dehydrobromination by treatment with Li_2CO_3 yielded the Δ^7-6-oxosteroid (XLIII). The 14α-hydroxy-group was introduced into the latter by conversion into the enol acetate (XLVI) (acetic anhydride and perchloric acid) and its oxidation with monoperphthalic acid. The acetate groups in the resulting product (XLVII) were hydrolysed on heating under mild alkaline conditions (K_2CO_3–H_2O–CH_3OH) and there was inversion at C-5 with formation of compound (XLVIII). For conversion into α-ecdysone (II), this compound required only the attachment of the side chain, which was achieved by a Grignard reaction via the lactone group with a large excess of CH_3MgBr. 22-iso-α-ecdysone was synthesised according to a similar scheme from the 22*S*-lactone, which is isomeric with compound (XLV).[182] The scheme for the synthesis of the ecdysone nucleus described in the above studies has also been applied in the synthesis of rubrosterone[183].

The synthesis of ecdysterone (VI) by the same group of investigators[184] begins with pregnenolone, which was converted in nine stages into compound (XLIX) (the introduction of the 2β,3β-diol group was achieved via the 3,6-diketone, as in the synthesis of α-ecdysone[35]). Acetylation, bromination, and dehydrobromination made it possible to obtain from (XLIX) the Δ^7-6-oxosteroid (V) into which the 14α-hydroxy-group was introduced by oxidation of the enol acetate with monoperphthalic acid. Alkaline isomerisation at C-5, protection of the diol group in the A ring by the formation of an acetonide, and oxidation at C-20 with the CrO_3–pyridine complex yielded the 20-ketone (LI), which has all the structural elements of ecdysterone except for the side chain. The latter was built up in five stages. The Normant reaction and the corresponding ozonolysis of the resulting vinylmethanol (LIV) gave the aldehyde (LIII), which was introduced into a Grignard reaction with the MgBr derivative of the THP ether of 2-methylbut-3-yn-2-ol, forming compound (LII). Hydrogenation of the triple bond, hydrolysis of the protecting groups, and chromatographic separation of the C-22 isomers formed yielded ecdysterone (VI), which was identical with the natural hormone.

The third scheme for the synthesis of ecdysones described above begins directly with 22-aldehydes, which facilitates the introduction of the side chain. Its principal disadvantage is the large number of stages involved in the introduction of the 2,3-diol group and the side chain.



The synthesis of α-ecdysone (II) from ergosterol (LV) with introduction of the structural elements according to the scheme *3 → 1 → 5 → 4 → 2* developed by Swiss chemists is free from the majority of the disadvantages of the schemes for the synthesis of ecdysones discussed above[154,155]. Oxidation of ergosteryl acetate with CrO_3 gives the 5α-hydroxy-6-oxo-derivative, which on reduction with zinc dust in acetic acid is converted into compound (LVI) in which the Δ^7-6-oxo-structure is already formed[185]. Further synthesis was performed via several pathways, of which only one proved to be successful. The two-stage substitution of the 3β-acetoxy-group in compound (LVI) by the 3β-methanesulphonyloxy-group with subsequent cleavage of the methanesulphonate with Li_2CO_3 gave the Δ^2-steroid (LVII). *cis*-Hydroxylation of the Δ^2-bond (silver acetate and iodine), protection of the resulting 2β,3β-diol group by formation of the diacetate, and ozolysis under controlled conditions resulted in the stereospecific formation (without inversion at C-20) of the 22-aldehyde (LX). Treatment of this aldehyde by the Grignard reagent obtained from the THP derivative of 2-methylbut-3-yn-2-ol led to a mixture of isomeric 22ξ-hydroxy-derivatives in which the required 22*R*-component (LIX) predominated; the mixture was separated by chromatography on silica. Catalytic reduction of the triple bond in the C-23–C-24 position¶ and subsequent introduction of the 14α-hydroxy-group by treatment with SeO_2 yielded compound (LVIII). Isomerisation at C-5 and hydrolysis of the acetoxy-groups under mild alkaline conditions (K_2CO_3–H_2O–CH_3OH) gave the corresponding 2β,3β-diol with the *cis*-junction of the A and B rings and hydrolysis of the THP group with dilute HCl yielded α-ecdysone (II). The above scheme constitutes the simplest procedure for the synthesis of ecdysones: the conversion of ergosterol (LV) into α-ecdysone (II) requires 14 stages in this scheme. The yield of compound (LVIII) is 0.063% with respect to ergosterol[155] (the yields in the last two stages are not indicated).



In the other versions of this scheme for the synthesis of α-ecdysone, the order of introduction of the principal structural elements of the molecule was altered[155]. For example, an attempt was made to achieve the isomerisation at C-5 already in the stage of the 2β,3β-diol obtained by the hydroxylation of the Δ^2-steroid (LVII); however, this involves also isomerisation at C-14 to the *cis*-C/D derivative. Evidently, before isomerisation at C-5 it is necessary to protect the C-14 position by introducing a 14α-hydroxy-group into the molecule. At the same time

¶The use of tritium instead of hydrogen in the hydrogenation of compound (LIX) (and other intermediates with a triple bond in the side chain obtained by other procedures) leads to α-ecdysone and its 25 deoxy-derivative (formed as a side product), labelled with tritium at C-23 and C-24; these compounds have been used in biological studies[49,180].

the introduction of this group before constructing the side chain caused an undesirable alteration in the stereochemistry of the Grignard reaction: the 14α-hydroxy-analogue of the aldehyde (LX) gave rise only to the 22*S*-isomer, which was converted in two stages as in the synthesis described above, into 22-iso-α-ecdysone. Thus in this case it is necessary to introduce initially the side chain into the molecule, then the 14α-hydroxy-group, and the isomerisation at C-5 must be carried out only in the last stage (i.e. the structural fragments must be introduced according to the scheme *5* → *4* → *2*). This is evidence of a considerable importance of the correct choice of the sequence of stages in the synthesis.

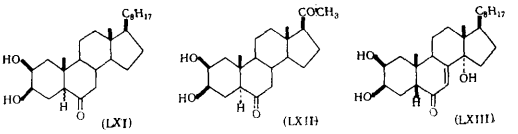
IV. ANALOGUES OF ECDYSONES

The study of analogues of ecdysones is of great practical importance, since these substances, which act as insecticides and chemosterilants, make it possible to control the numbers of insect pests. In the first place it is necessary to examine the effect of the structure of ecdysones on their MMH activity, which permits the elucidation of the relative importance of various structural elements of the molecule for its biological activity.

At the present time, the role of the hydroxy-groups in the steroid skeleton and in the side chain of ecdysones has been mainly investigated. The importance of the hydroxy-groups in the A ring of the ecdysone molecule can be assessed from the following facts: while the activity of 2-deoxyecdysterone, which has a 3β-hydroxy-group, is equal to that of ecdysterone [124], its 3α-epimer is three times less active [186]. Thus the hydroxy-group at C-2 is of no importance for MMH activity, while the presence of the hydroxy-group at C-3 and its equatorial configuration play a significant role. The importance of the 14α-hydroxy-group is even greater, its removal lowering the activity by a factor of 15 compared with α-ecdysone [187]. The introduction of an additional 5β-hydroxy-group into the molecule (polypodine B) greatly increases the MMH activity [128].

The presence in the steroid molecule of a long side chain at C-17 is necessary for MMH activity, since rubrosterone and its analogue with an acetyl side chain (VIII) do not show this activity [112, 120]. The complete absence of a hydroxy-group from the side chain also sharply reduces the activity (by a factor of 50 compared with α-ecdysone [187]). The removal or isomerisation of the 22*R*-hydroxy-group leads to a sharp fall or complete disappearance of MMH activity [111,155,170]; the introduction of an additional 26-hydroxy-group has the same consequences [126]. On the other hand, an additional 24-hydroxy-group or a Δ^{24}-bond do not have a significant effect on the activity, while a 20*R*-hydroxy-group increases it somewhat [134,135]. The presence of an ethyl-group at C-24 in 29C-ecdysones does not affect the activity [139,149]; nor is the activity reduced in the presence in the side chain of lactone groups (capitasterone, cyasterone) [113,148]. At the same time an epoxy-group in the side chain (stachysterone D) virtually eliminates the MMH activity of the compound [135].

Many synthetic analogues of ecdysones can inhibit the moulting and metamorphosis in the development of insects (i.e. they can act as ecdysone antagonists); also they can have a general toxic effect on adult forms. The toxic effect of ecdysone analogues—derivatives of androstane, pregnane, and cholestane—was investigated on the bug *Pyrrocoris apterus* [188-190] and certain other insects [174]. Compounds (LXI)-(LXIII) proved to be the most active.



(LXI) (LXII) (LXIII)

Compounds with a low MMH activity are the most toxic for insects and conversely. The presence of a hydroxy-group at C-2 and the configuration of the hydrogen atom at C-5 proved to be unimportant for toxicity. The toxicity fell somewhat on introduction of a Δ^7-bond and disappeared completely on acetylation of the 3-hydroxy-group or on reduction of the 6-oxo-group. At the same time it was not possible to establish a definite link between toxicity and steroid structure: probably in this case there is a superposition of various toxic effects, which depend in different ways on the structure. The direct cause of the death of *P. Apterus* larvae proved to be the breakdown of the integrity of the cell membranes in consequence of a change in the surface tension of the haemolymph caused by the introduction of the steroid [189]. It is noteworthy that the susceptibility of different insect species to steroid insecticides is variable [67,74]. This necessitates a large-scale programme of tests in each case and at the same time leads to the possibility of choosing compounds which selectively supress a given insect species.

The observation of a sterilising effect by many ecdysone analogues on the females of the housefly and other Diptera is also of considerable interest [74,191,192]. It was not possible to observe rigorous correlations between structure and activity in this case either, but the presence of a 6-oxo-group in the steroid molecule is apparently necessary both for sterilising activity and for toxicity. Synthetic analogues of ecdysones are a new class of specific insect chemosterilants, which are safe for warm-blooded animals [193].

Thus synthesis of ecdysone analogues gives rise to the possibility of fundamentally new hormonal insecticides. One may expect that, apart from their high activity, these compounds will exhibit selectivity of action in relation to a chosen insect species and that insect pests will be unable to adapt to these insecticides.

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Investigation of Keto-Enol Tautomerism by Nuclear Magnetic Resonance Spectroscopy

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The review considers methods for the determination of tautomeric composition from NMR spectra and gives a systematic account of the results of studies on keto-enol tautomerism. The bibliography includes 160 references.

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I. INTRODUCTION

The introduction of physical (primarily spectroscopic) methods into organic chemistry made it possible to achieve in a short period considerable advances in the study of the phenomenon of tautomerism. The most recent of these methods (nuclear magnetic resonance) is the most promising and offers universal procedures for such investigations. High-resolution NMR spectra yield a wide variety of information about a tautomeric system: the chemical and steric structures of the tautomers, the positions and strengths of hydrogen bonds, the amounts of different tautomers, and the rate and mechanism of their interconversion. The advantages of the NMR method and the interest in tautomeric problems—a field which allows a wide scope for the application and verification of the fundamental concepts of organic chemistry [1-2]—resulted in a rapid growth of the number of relevant publications (from a few in 1960† to hundreds at the present time). Despite the evident interest of the investigators of tautomerism in NMR spectroscopy, there are no reviews in either Soviet or foreign literature giving a systematic account of the results from the large-scale application of NMR in the study of tautomerism in the last few years.

The available review literature comprises short illustrative chapters in certain monographs [4-9] and papers [10-15]. In the present review an attempt has been made to fill this gap and to describe the advances in the field of tautomerism made using NMR. Within the limits of a single review, it is not possible to examine in sufficient depth the NMR studies on tautomerism of all types. The authors restricted themselves to prototropic‡ tautomerism as a result of the migration of a proton between carbon atoms and a heteroatom (N, O, S) or between two heteroatoms.

† The first study in which NMR was employed to investigate tautomerism was published in 1953 [3].

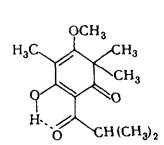
‡ NMR has been successfully employed to investigate the prototropic tautomerism associated with the migration of a proton between carbon atoms and also various types of non-protrotopic tautomerism [15].

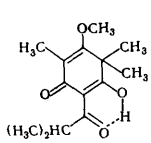
In the discussion of the tautomerism of various classes of organic compounds attention has been concentrated on the equilibrium tautomeric composition and the factors which determine it. The chemical shifts are quoted on the τ-scale.

II. METHODS OF ANALYSIS OF TAUTOMERIC SYSTEMS BY NMR SPECTROSCOPY

In slow tautomeric transformations, which satisfy the inequality $1/t_A + 1/t_B \ll |\nu_A - \nu_B|$ (ν_A and ν_B are the NMR signal frequencies and t_A and t_B are the average lifetimes of the tautomers A and B), the NMR spectra of forms A and B can be observed separately and the tautomeric composition can be readily determined from the intensities of the corresponding spectral lines (to within 1%) [4-8].

Thus in the NMR spectrum of the natural dye tasmanone dissolved in $CDCl_3$ [16] the signals of all the methyl groups consist of two very close components with an intensity ratio of 1 : 1.9 and in addition there are two signals due to the chelate enolic protons (−9.4 and −8.7 p.p.m.). The lines merge when the solution is made alkaline but the splitting reappears on neutralisation of the added alkali. This leads to the conclusion that the system consists of a mixture of two enolic tautomeric forms (1A and 1B)§, the rate of the interconversion of which is greatly accelerated in the presence of a base, which increases the concentration of the anion.


(IA)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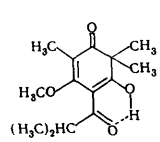
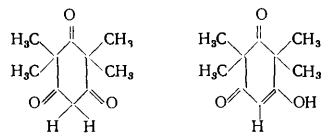

(II)

§ This rules out the alternative structure of tasmanone, in which there is only the enolic form (II).

The next stage of the analysis, involving the assignments of the spectral lines to specific tautomeric forms, is based on the ^{1}H NMR data for tetramethylphloroglucinol (III)—a model compound. These data show that the enolisation of the carbonyl group leads to the descreening of the adjacent geminal methyl groups. Therefore the low-field (less intense) signal of the corresponding groups of tasmanone was assigned to form (IB). Clearly the other less intense signals are also due to the form (IB), the content of which is 35%.



(IIIA) (IIIB)

If the interconversions of tautomers A and B take place at a frequency exceeding $|\nu_A - \nu_B|$, their NMR signals merge and are characterised by an average chemical shift $\tau = p_A\tau_A + p_B\tau_B$, where τ_A and τ_B are the chemical shifts¶ and p_A and p_B the fractions of forms A and B ($p_A + p_B = 1$). A similar expression is valid also for the spin–spin coupling constants (SSCC):† $J = p_AJ_A + p_BJ_B$.[4-8] In this case the fraction of any form (for example A) is found from the following formulae:

$$p_A = (\tau - \tau_B)/(\tau_A - \tau_B), \quad (1)$$

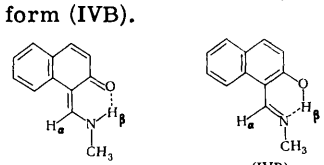
$$p_A = (J - J_B)/(J_A - J_B). \quad (2)$$

The case where appreciable spin–spin coupling obtains between the given nuclei in only one tautomer is frequently encountered (for example, $J_B = 0$). Then

$$p_A = J/J_A. \quad (3)$$

The accuracy of the determination of the proportions of tautomers in fast tautomeric interconversions is much lower than in slow interconversions. The absolute error for p_A and p_B amounts at best to several per cent. The principal sources of error are the inaccuracies in the values of τ_A, τ_B, J_A, and J_B, which are usually assumed equal to the corresponding values for model non-tautomeric compounds. In certain studies[17,18] corrections have been applied for the change in the chemical shifts in ^{1}H NMR on methylation of aromatic and heteroaromatic compounds at the oxygen and nitrogen atoms, which permits a more accurate prediction of the values of τ for the tautomeric forms modelled.

As an example, we shall determine the tautomeric composition of the Schiff base (IV). The $H_\alpha - H_\beta$ spin–spin coupling constant is close to 13 Hz‡ for form (IVA) and is zero for form (IVB).



(IVA) (IVB)

¶ In this review the proton chemical shifts are expressed on the τ-scale (p.p.m.)[5].

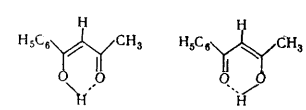
† The interaction of nuclei not involved in rapid intermolecular exchange is considered here. Otherwise the splitting of the NMR signals due to spin–spin coupling is not observed.

‡ This value is characteristic of the *trans*-form of the fragment =CH–XH, where X = O [19] or NR.[20]

Measurement of $J_{\alpha\beta}$ (9.8 Hz at 0°C in $CDCl_3$) makes it possible to estimate by Eqn. (3) the content of form A (75%). A similar value (83% of A) was obtained by comparing the $H_\beta - NCH_3$ spin–spin coupling constant (4.6 Hz) with the corresponding values for forms A (5.5 Hz) and B (0 Hz). Finally, more accurate data can be obtained from the ^{15}N–H spin–spin coupling constant. For the aminoketone forms, J_{NH} is close to 95 Hz and is zero for the iminoenol forms. The observed value of J_{NH} for (IV) is 72.3 Hz, which corresponds to 76% of form A [20,21].

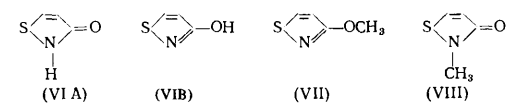
The problem of the short-lived internal tautomers A and B of benzoylacetone and other β-diketones cannot be readily solved with the aid of ^{1}H NMR spectroscopy, since the chemical shifts of the stable protons differ only slightly for the two forms and the values of τ_{OH} for these forms are unknown. The ^{17}O NMR spectra are more informative[22,23]. The ^{17}O nuclei of the carbonyl groups absorb near 495 p.p.m. and those of the enol groups near 35 p.p.m. relative to the signal for water (data from the spectra of model compounds).

In acetylacetone, where the enolisation of a given carbonyl group is equally probable, the average ^{17}O chemical shift is 265 p.p.m. However, the ^{17}O signal of the benzoyl group of benzoylacetone (V) is displaced towards higher fields (230 p.p.m.), which indicates the presence of an excess of tautomer A. Using Eqn. (3), it is possible to estimate the tautomeric composition (56% of A and 44% of B). The acetyl oxygen signal is displaced towards low fields (300 p.p.m.) in accordance with the lower probability of the enolisation of this group:



(VA) (VB)

In conclusion we shall quote an example of the determination of tautomeric compositions from the chemical shifts and spin–spin coupling constants of stable protons. 3-Hydroxyisothiazole in dimethyl sulphoxide exists as a mixture of forms (VIA) and (VIB), which are rapidly interconverted. The average chemical shifts and spin–spin coupling constant of the protons in the 4- and 5-positions (3.41 and 1.22 p.p.m.; 5.1 Hz) are closer to those for the fixed-configuration compound (VII) modelling form (VIB) (3.25 and 1.12 p.p.m.; 4.7 Hz) than to the values for the model compound (VIII) (3.81 and 1.55 p.p.m.; 6.3 Hz). Calculations by formulae (1) and (2) agree and show that the fraction of form (VIB) is 75%: [24]



(VI A) (VIB) (VII) (VIII)

In many cases the presence of a small amount of one of the tautomeric forms, the NMR signals of which cannot be observed, can be detected indirectly, namely from the deuterium exchange involving this form. Thus measurements by ^{1}H NMR spectroscopy of the rate of deuteration of the alkyl groups of ketones, which like bromination proceed via the enol form, not only makes it possible to confirm the presence of the enol but also allows the determination of the predominant enolisation pathway in asymmetric ketones.

For example, 4,4-dimethyl-2-pentanone (IX) can exist in two enolic forms.

$H_3C-CO-CH_2-C(CH_3)_3$ (IX A) $H_2C=C(OH)-CH_2-C(CH_3)_3$ (IXB) $H_3C-C(OH)=CH-C(CH_3)_3$ (IXC)

The rate constants for the deuterium exchange involving the methyl (8.1×10^{-6} s^{-1}) and methylene (2.4×10^{-6} s^{-1}) groups were determined from the decrease of the methyl and methylene group signal intensities in the ^1H NMR spectrum as a result of the deuteration of forms (IXB) and (IXC). These data show that the preferred enolic form is (IXB) [25]. An analogous procedure may be employed in more complex cases [26].

The NMR method permits a quantitative estimation of the rates of both rapid and slow chemical reactions [4,5,27-31], in particular tautomeric transformations [27,32-34]. The methods used in such estimations differ, depending on the rate of interconversion of the tautomeric forms.

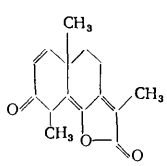
III. KETO-ENOL TAUTOMERISM

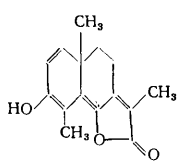
1. MONOCARBONYL COMPOUNDS

In the simplest ketones enolisation is slight [35] and cannot be detected directly by spectroscopic methods. Nevertheless, the presence of the enolic form can be deduced indirectly from the deuteration of α-carbon atoms, which proceeds via the enolate anion or the enolic form.

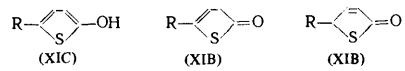
Rappe and Sachs [25,36-40] and other workers [41-45] measured the rate constants for deuterium exchange from ^1H NMR spectra, determined the predominant enolisation pathway for a number of asymmetric ketones, and investigated the effect of the solvent on the rate of deuterium exchange. In particular, it was shown that enolisation takes place most readily in the direction of the methyl group and least so in the direction of the methylidyne group of ketones.

In more complex systems where enolisation leads to the formation of conjugated bonds, the content of the enolic form may prove to be significant and susceptible to direct measurement. Thus the contents of the keto-form (XA) and enol form (XB) of santonin (X) and dihydrosantonin were determined from the intensities of the corresponding ^1H NMR lines in various solvents [46]. Santonin (100% of the keto-form in the crystalline material) is enolised very weakly in chloroform (less than 5%) and considerably in methanol (39%) and pyridine (70%). Dihydrosantonin (100% enol in the solid state) is almost completely enolised in pyridine and less so in methanol (84%) and chloroform (43%). The shift of the equilibrium towards the enol in proton-accepting solvents is probably associated with the formation of an intermolecular hydrogen bond stabilising the enolic form. The keto-enol interconversion in santonin takes place at low rates, which is indicated by the slow substitution of the proton at C-4 by deuterium in the presence of D_2O even at high temperatures.


(X A)


(X B)

Hörnfeldt investigated the tautomerism of various hydroxythiophens [47-49]. ^1H NMR spectra revealed 25-30% of the hydroxy-form (XIA) of 5-aryl- and 5-thiono-2-hydroxythiophens (XI) in methanol, whereas in carbon tetrachloride this form was absent.

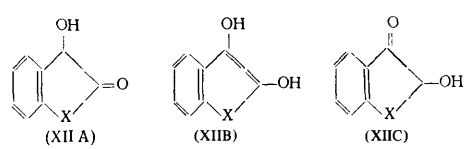

(XIC) (XIB) (XIB)

Form (XIA) was not detected in 5-alkyl-substituted 2-hydroxy-thiophens. In the presence of catalytic amounts of acids or bases, there is a rearrangement to an equilibrium mixture of the keto-forms (XIB) and (XIC), the composition of which depends on the hyperconjugation effect of the substituent and on the polarity of the solvent. The kinetics of the rearrangement (XIB) $\rightleftharpoons$ (XIC) have been investigated [47,48].

In alkyl-substituted 3-hydroxythiophens, the hydroxy-form (enol) is present in considerable amounts even in a non-polar solvent (carbon disulphide) (80, 55, and 30% for 5-methyl-, 5-t-butyl-, and 2,5-dimethyl-derivatives respectively). The chemical shifts of the signal due to the enolic proton are in the range between 3.3 and 3.8 p.p.m. [47]; 2- and 3-mercaptothiophens exist in the thiol form [50].

3-Hydroxythionaphthene was investigated by two groups of workers [51-53]. Their results show that the freshly sublimed substance exists entirely in the keto-form.

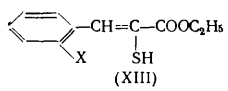
Sterk et al. [54] showed that in polar solvents the lactone of *o*-hydroxymandelic acid exists in the 3-oxo-form (XIIC, X = O). The 2-oxo-form (XIIA, X = O) predominates in non-polar media at high temperatures. The dienol form (XIIB, X = O) form was not detected.


(XII A) (XIIB) (XIIC)

In dihydroxyindole solutions in bromoform there is an equilibrium between forms (XIIA, X = NH) and (XIIB, X = NH), which on raising the temperature is displaced towards the dienol form (XIIB, X = NH).

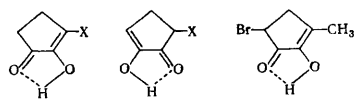
2. α-DICARBONYL COMPOUNDS

Acyclic 1,2-dicarbonyl compounds are as a rule weakly enolised. However, some of their aryl-substituted derivatives may contain significant amounts of the enolic form in a slow equilibrium with the diketo-form [55]. The ^1H NMR spectra show that, in contrast to pyruvic acid and its esters which do not contain an enolic form [56], aryl-substituted derivatives of thiopyruvic acid (XIII, X = H, CH_3, or Cl) exist largely in the thiol form [57]:


(XIII)

The degree of enolisation of cyclic α-diketones depends on ring size. The smaller the ring the more pronounced is the electrostatic repulsion between the adjacent dipoles of the carbonyl groups, which reduces the stability of the diketo-form [58].

Five-membered α-diketones are as a rule completely enolised in non-polar solvents as well as in aqueous solutions[58,59]. The ^{1}H NMR spectrum of 3-methylcyclopentane-1,2-dione in chloroform[60,62] not only fully confirms complete enolisation but also gives information about its direction. The absence from the spectrum of the vinyl proton signal and the chemical shift of the unsplit methyl group signal (8.07 p.p.m.)[61] support the structure (XIVA, X = CH_3). The structure (XIVA, X = Br) was also proved for 3-bromocyclopentane-1,2-dione, which is completely enolised in acetone[62]. 5-Bromo-3-methylcyclopentane-1,2-dione exists in acetone in the enolic form (XV)[58].



(XIVA) (XIVB) (XV)

3-Bromo-3-methylcyclopentane-1,2-dione, which exists in the diketo-form in a freshly prepared acetone solution, is gradually converted into the enolic form[15], the enolisation being accompanied by the migration of the halogen from the 3-position to the 5-position[62].

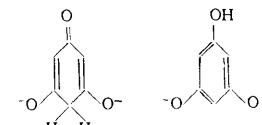
Six-membered cyclic α-diketones contain the diketo-form in addition to the enolic form[9,63]. Judging from the ^{1}H NMR spectra, in dilute aqueous solutions cyclohexane-1,2-dione is enolised approximately to the extent of 50%[64]. The rate of the keto–enol transformation is low but increases in the presence of acids and alkalis. At the same time there is a marked shift in the tautomeric equilibrium. Bakule and Long[64] determined the enthalpy and entropy of the keto–enol transformation in an aqueous medium (6 kcal mole^{-1} and −21 e.u. respectively). According to ^{1}H NMR and ^{17}O NMR data, in benzene cyclohexane-1,2-dione is completely enolised and the rate of exchange between the two equivalent enolic forms is low[22]. In the first case a distinct triplet due to the vinyl protons is observed and in the second case the individual signals of equal intensity due to the carbonyl and hydroxyl oxygen atoms. Freshly prepared cyclohexane-1,2-dione is fully enolised, but after two days 14% of the diketo-form appears[61].

Seven-membered cyclic α-diketones exist predominantly in the diketo-form[55]. In contrast to β-diketones (see below), α-diketones cannot form a mesomeric monoanion common to the two enolic forms; the interconversion of these enolic forms can therefore only occur via the diketo-form. The rates of these transitions are determined by the rates of their keto–enol interconversions, which are slow under the usual conditions. Chemical shifts of the enolic protons of α-diketones are in the range of positive values of τ. For example, τ_{OH} = 3.38 p.p.m. for 3-methylcyclopentanedione in chloroform[61]. This shows that the intramolecular hydrogen bond of the five-membered chelate ring is weak[5].

3. PHENOLS AND SIMILAR COMPOUNDS

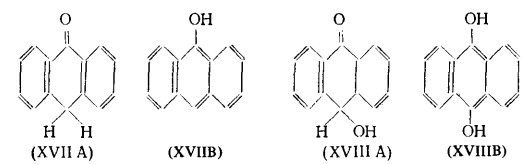
Phenols may be regarded as specific keto–enol systems[9,65]. However, the amount of the keto-form of simple phenols, if it exists at all, is too small to be measured. The keto-enol interconversion is considered as one of the pathways of the exchange of aromatic protons for deuterons in pyrogallol and β-naphthol in an alkaline medium[66].

Forms other than enolic have not been detected for phloroglucinol (a pyrogallol isomer) and its monoanion. However, the dianion exists in the keto-form (XVIA)[65]. This conclusion was arrived at using data obtained by a number of methods, but the ^{1}H NMR spectra are the most convincing[67]. The aromatic form of the dianion (XVIB) has not been detected in appreciable amounts.



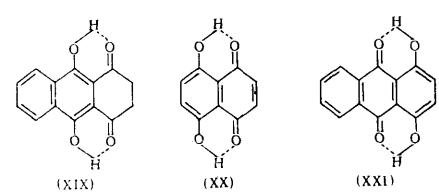
(XVI A) (XVIB)

Sterk investigated the effects of temperature on the anthrone (XVIIA)–anthrol (XVIIB) and oxanthrone (XVIIIA)–9,10-dihydroxyanthracene (XVIIIB) keto–enol equilibria in various solvents[68].



(XVII A) (XVIIB) (XVIII A) (XVIIIB)

The content of anthrone increases from 5% in bromoform to 50% in pyridine and 73% in dimethyl sulphoxide (at 40°C). The (XVIIIA) ⇌ (XVIIIB) equilibrium depends only slightly on the solvent (5–30% of the enol at 40°C) but is strongly displaced towards the enol (XVIIIC) when the temperature is raised. Dihydroquinizarin exists entirely in the diketo-form (XIX) regardless of the medium and temperature[68,69].

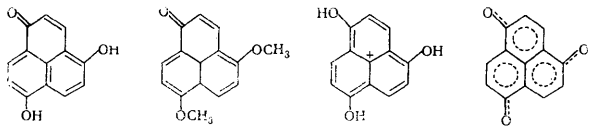


(XIX) (XX) (XXI)

Tautomerism associated with rapid migration of the proton involved in the intramolecular hydrogen bond between the oxygen atoms has been observed in 1,4-dihydroxynaphthoquinone (XX), in contrast to quinizarin, which exists in form (XXI)[69].

An unusual tautomerism was observed by the ^{1}H NMR method in 4,7-dihydroxyphenalenone (XXII)[70]. The spectrum of (XXII) should contain three quartets of type AB due to the three pairs of interacting aromatic protons in the three non-equivalent rings. Precisely this type of spectrum has been observed for 4,7-dimethoxyphenalenone (XXIII). The non-equivalence of the rings of (XXIII) is shown not only in different screening of the protons but also in different spin–spin coupling constants (J_{23} = 8.4 Hz, J_{56} = 9.2 Hz, and J_{89} = 10.1 Hz). However, the spectrum of (XXII) contains only one quartet, common to the three pairs of protons, which can be explained by the effective equivalence of all the rings achieved as a

result of the rapid interconversion of three equivalent structures of type (XXII).

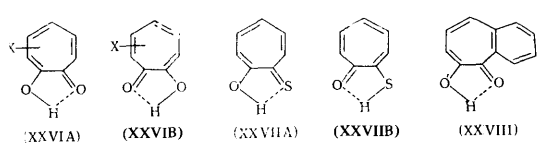


(XXII) (XXIII) (XXIV) (XXV)

This conclusion is confirmed by the value of J_{AB} for (XXII) (9.2 Hz), which is equal to the mean of the three J_{AB} constants for (XXIII). The first stage in these tautomeric transformations may be the formation of the cation (XXIV) or the dianion (XXV).

Tropolones (XXVI) (non-benzenoid aromatic α-diketones) are completely enclosed[71]. The ^{1}H NMR [71,72] and ^{17}O NMR [22] spectra confirm both their complete enolisation and the averaging of the electronic environments of the protons and oxygen nuclei in the left-hand and right-hand parts of the molecules of tropolone and its 5-substituted derivatives as a result of the rapid exchange between the equivalent enolic forms. The merging of the ^{17}O NMR signals of the hydroxy- and carbonyl groups indicates that the lifetimes of these forms are not more than 10^{-5} s. The rapid interconversion of the enolic forms of tropolones, in contrast to saturated α-diketones, is due to the presence of a mesomeric anion common to both enolic forms and reduces to the migration of a proton from one oxygen atom to the other with a corresponding π-electron shift.

In the case of asymmetrically substituted tropolones, the question arises of the preferential direction of enolisation, i.e. the proportions of forms (XXVIA) and (XXVIB). It has been shown[73] that the equilibrium in 3-bromotropolone is somewhat displaced towards the form (XXVIA, X = Br).



(XXVIA) (XXVIB) (XXVIIA) (XXVIIB) (XXVIII)

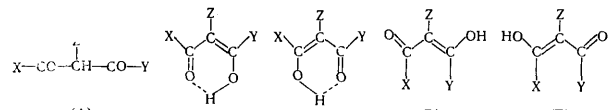
The enolic protons of tropolones in $CDCl_3$ and CCl_4 absorb in the range 0–3 p.p.m., i.e. they are more descreened than the enolic protons of saturated α-diketones. One cannot rule out the possibility that this effect is due not only to the descreening effect of the aromatic rings but also to the stronger intramolecular hydrogen bonds[71] in tropolones, the existence of which is indicated by infrared spectra[74].

Evidence of the predominance of the thiono-form (XXVIIA) of 2-mercaptotropolone (XVII) and its 4- and 6-alkyl-substituted derivatives has been obtained by ^{1}H NMR (in carbon tetrachloride) and other spectroscopic methods[75]. The chemical shift of the enolic proton[56] is 0.12 p.p.m.

In contrast to tropolone, 6,7-benzotropolone exists in form (XXVIII), in which the aromaticity of the benzene ring is unaffected[76].

4. OPEN-CHAIN β-DICARBONYL COMPOUNDS

In general β-dicarbonyl compounds, which include diketones, ketoaldehydes, ketoacids, and their esters and amides, may exist in five tautomeric forms: the diketo-form (A), two *cis*-enolic forms (B) and (C), and two *trans*-enolic forms (D) and (E). The reported presence of appreciable amounts of the dienolic form[77] has not been confirmed[78]. In water and alcohols the keto-form (A) can exist as hydrates and hemiacetals, readily revealed by the NMR method§.



(A) (B) (C) (D) (E)

The interconversion of structures (B) and (C) does not require the dissociation of the intramolecular hydrogen bond and reduces to the migration of a proton between two oxygen atoms. Therefore it is very rapid. The lifetime of the tautomer is less than 10^{-4} s.[33] All other tautomeric transformations in this system are as a rule slow. The half-life associated with the attainment of the keto–enol equilibrium at room temperature after separation of the tautomers amounts to minutes for acetylacetone[82], hours for α-phenylformylacetic acid esters[32], and days for β-carbonyldithioacid acid esters[83]. Thus in the general case the NMR spectra of the above tautomeric compounds should contain the individual signals of forms (A), (D), and (E) and the common signal of forms (B) and (C).

(a) Keto–enol Equilibrium

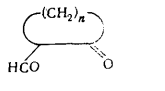
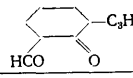
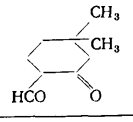
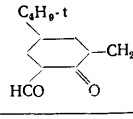
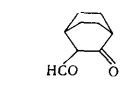
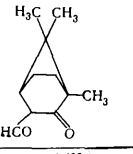
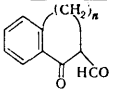
Here we shall consider the effect of molecular structure, temperature, and medium on the position of the keto–enol equilibrium, i.e. on the contents of forms (A) and (B $\rightleftharpoons$ C). The presence of *trans*-enolic forms is observed only in rare cases, which will be discussed separately.

Effect of structural factors and temperature (Tables 1–11). According to NMR data, malonodialdehyde and almost all the aldoesters and ketoaldehydes investigated are completely enolised in both non-polar solvents and as pure liquids (Table 1). On passing from ketoaldehydes to the corresponding diketones and particularly to ketoesters and ketoamides, the percentage of enol falls. For example, in carbon tetrachloride the fractions of the enolic form of acetoacetaldehyde, acetylacetone, acetoacetic ester, and the *N*-benzylamide of acetoacetic acid (in $CDCl_3$) are 100%,[79] 94% [100], 20% [108], and 5% [120] respectively. This effect is associated with the increasing electron density at the carbon atom of the carbonyl group in the above series and the corresponding decrease of the ionisation constants of the dicarbonyl forms[1,9]. It is noteworthy that the ester and amide groups are hardly enolised, in conformity with their low tendency towards nucleophilic addition reactions involving the carbonyl group. The failure of malonic ester to enolise[9] and the increasing degree of enolisation with increasing electron-accepting capacity of the substituents X and Y are consistent with this view[94,121] (Tables 2–4 and 9). A satisfactory linear corelation between the fraction of the enolic form and Hammett's σ constants and particularly Brown's σ^+ constants has been observed for

§ The presence of 76% of the hydrated keto-form of formylacetone in aqueous solution has been demonstrated[79]. For a number of trifluoro-β-diketones in water and alcohols, an equilibrium between the enolic and hydrated or hemiacetal forms has been observed[80,81].

meta- and *para*-substituted benzoyl derivatives of acetic ester[99], acetophenone[94], cyclohexanone[122], and cyclopentanone[121].

Table 1. The screening of the enolic and aldehyde protons, the constants for the spin–spin coupling between them, and the mode of enolisation of β-dialdehydes, β-ketoaldehydes, and β-aldoesters (A ⇌ B, Y = H)[a].

Compound	Medium	τ OH p.p.m.	τCHO, p.p.m.	J, Hz	[B]/([B]+[C])%	Refs.
OHC–CH_2–CHO	$CDCl_3$	−0.08	1.60	—	50	84 (79, 85)
OHC–CH(CH_3)–CHO	$CDCl_3$	0.61	—	—	50	85
OHC–CH(C_6H_5)–CHO	CCl_4	−4.10	1.35	—	50	86
H_3CCO–CH_2–CHO[b]	$CDCl_3$	−3.58	2.13	—	—	79 (84)
H_3CCO–CH(C_6H_5)–CHO	CCl_4	−5.40	1.85	6.3	—	86
OHC–CH(C_6H_5)–$COOCH_3$[b]	$CDCl_3$	−2.20	2.55	13.3	100	32
OHC–CH(C_6H_5)–$COOC_2H_5$	$CDCl_3$	−2.40	2.45	13.3	100	32 (86)
 $n = 3$[b]	CCl_4	−1.35	2.73	—	78	19 (87, 88)
$n = 4$	CCl_4	−4.27	1.39	3.4	24	19 (86, 87)
	C_6H_6	—	—	—	33	22
$n = 5$	CCl_4	−4.60	2.43	8.0	66	19 (87)
$n = 6$	CCl_4	−4.97	1.89	5.8	44	19
$n = 7$	CCl_4	−5.14	1.57	—	31	19
$n = 8$	CCl_4	−5.11	1.24	—	18	19
$n = 10$	CCl_4	−5.15	1.49	—	28	19
	CCl_4	—	1.49	—	28	19
	CCl_4	—	2.57	9.8	71	19
	CCl_4	—	1.05	1.3	10	19
 b	CCl_4	−2.15	2.98	—	88	19
 b.c.	CCl_4	−0.15	3.29	12	100	19
 $n = 1$	C_6H_6	—	—	—	87	22
$n = 2$	CCl_4	−2.24	2.40	—	—	87
$n = 3$	CCl_4	−4.74	1.84	—	—	87
	CCl_4	−4.20	2.05	—	—	87

a. The values of τ and *J* quoted in the studies for which the references are enclosed in brackets are close to those in the Table.
b. Several per cent of the formylketone form was observed. All other compounds were fully enolised.
c. 5% of the *trans*-enolic form was detected.

Enolisation is also promoted by the increasing size of the terminal substituents X and Y (Tables 3 and 10), which is apparently due to the instability of the diketo-form owing to the steric interactions between the substituents[95]. Burdett and Rogers[95] attribute to this interaction the lower degree of enolisation of ketoesters compared with diketones. Indeed in ketoesters the alkyl substituent and the carbonyl group are separated by the small oxygen atom and the steric interaction is weakened. However, for large alkyl substituents, such as t-butyl, the stability of the diketo-forms falls and the percentage of the enol increases (Table 3). Such behaviour is characteristic also of ketoamides[124].

Table 2. The content of the enol and the screening of the enolic protons in the series of diketones R–CO–CH_2–CO–R′ in carbon tetrachloride.

R	R′	Enol, %	τ_{OH}, p.p.m.	Refs.
CH_3	CH_3	94	−5.4	89 (90)
t-C_4H_9	CH_3	—	−5.90	91
Mesityl	CH_3	—	−5.40	91
2-Thiono	CH_3	—	−5.66	91
CF_3	CH_3	100	−4.24	90
C_6H_5	CH_3	94.5 (90.5 *)	−6.16 (−6.27 *)	92 (91, 93)
p-N(CH_3)$_2$$C_6H_4$	CH_3	77.5*	−6.52*	94
p-$OCH_3C_6H_4$	CH_3	94.7	−6.16	93
p-$CH_3C_6H_4$	CH_3	95.7	−6.00	93
p-BrC_6H_4	CH_3	100	−6.03	93
p-$NO_2C_6H_4$	CH_3	100	−5.92	93
t-C_4H_9	t-C_4H_9	100	−6.30	91
C_6H_5	t-C_4H_9	100	−6.70	91
C_6H_5	CF_3	100	−4.60	91
CF_3	CF_3	100	−3.00	90
CF_3	C_6H_5	100	−7.00	91 (90, 93)
2-Thiono	2-Thiono	100	−6.20	90

* In $CDCl_3$.[94]

Table 3. Enolisation and the screening of the enolic protons of β-ketoesters R–CO–CH_2–COOR′ (pure liquids).

R	R′	Enol, %	τ_{OH}, p.p.m.	Refs.
CH_3	C_2H_5	6–8	−2.17	95, 96, 97
CH_2Br	C_2H_5	6	−1.87	95
CH_2F	C_2H_5	7.2	—	96
CHF_2	C_2H_5	53	—	96
CF_3	C_2H_5	89	−2.00	95, 96
C_6H_5	C_2H_5	22	−2.83	95, 98
CH_3	CH_3	0	—	95
CH_3	n-C_4H_9	15	−2.17	95
CH_3	t-C_4H_9	17	−2.22	95

The α-substituent (Z) has a very marked influence on the keto–enol equilibrium (Tables 5, 6, 8, and 10). Electronegative substituents increase sharply the degree of enolisation. α-Alkyl substituents cause a marked decrease of the percentage of enol. However, here the cause is mainly steric—repulsion between the α- and ring substituents, which makes the chelate ring of the *cis*-enolic form unstable. For example, whereas dibenzoylmethane is fully enolised, its α-methyl analogue exists exclusively in the diketo-form[100]. The replacement of the oxygen of the carbonyl group by sulphur leads as a rule to almost complete enolisation (Tables 7 and 8)[110,125–127]. In alicyclic β-ketoesters the degree of enolisation depends in a complex manner on ring size (Table 7). Possibly this is due to conformational changes on passing from one ring to another[108,109].

A strong intramolecular hydrogen bond is also an important factor stabilising the *cis*-enolic form. The weakness of the intramolecular hydrogen bond in five-membered alicyclic compounds accounts for the relatively low degree of their enolisation (Tables 1 and 7).

With increase of temperature, the content of the enol falls. The thermodynamic parameters of enolisation have been determined for a number of β-dicarbonyl compounds by the NMR method (Table 10). The energy gain on formation of an intramolecular hydrogen bond ($\Delta H < 0$) promotes enolisation but, in view of the higher entropy of the keto-form ($\Delta S < 0$), the latter is not only present in significant amounts in a number of systems but actually predominates[55,78]. Ultimately the position of tautomeric equilibrium is determined by the competing energy and entropy factors. Table 10 shows that the enthalpy of enolisation (ΔH) increases with the dimensions of the terminal substituents and falls with increasing size of the α-substituent.

Table 4. The content of the enol[99] and the screening of the enolic protons[93] of *para*-substituted derivatives of benzoylacetic ester $XC_6H_4-CO-CH_2-COOC_2H_5$ in $CDCl_3$.

X	Enol, %	τ_{OH}, p.p.m.
OCH_3	3	−2.96
H	15	−2.93
Br	—	−2.93
Cl	23	−2.94
NO_2	53	−2.92

Table 5. Enolisation and the screening of the enolic protons of α-substituted acetylacetone derivatives $CH_3-CO-CHZ-CO-CH_3$ (pure liquids).

Z	Enol, %	τ_{OH}, p.p.m.	Refs.	Z	Enol, %	τ_{OH}, p.p.m.	Refs
H	81	−5.56	95, 100	C_6H_5[a]	~100	−6.60	91, 103
CH_3	30	−6.50	95, 100	Br	46	−5.36	95
C_2H_5	26	−6.80	101			(−5.80[a])	
n-C_3H_7	27	−6.80	101	Cl	94	−5.58	95, 100
iso-C_3H_7	0.1	−7.30	102	CN[a]	~100	−6.80	104
s-C_4H_9	0.7	−7.50	102	$COCH_3$[b]	100	−7.41	105
OCH_3[a]	—	−4.09	103	$COOCH_3$[a]	100	−8.62	106
$OCOCH_3$[a]	20	−4.35	103				

a. In carbon tetrachloride.
b. In $CDCl_3$.

Effect of the medium. On dissolution in solvents of low polarity, the percentage of the less polar *cis*-enolic form increases. Conversely polar solvents displace the equilibrium towards the polar diketo-form (Table 11). This can be explained by the solvation of the carbonyl groups by the polar solvent molecules, which increases the stability of the diketo-form[97,100,118]. Thus in dimethyl sulphoxide the enthalpy of enolisation (ΔH) of acetylacetone is lower by more than 1 kcal mole^{-1} compared with pure acetylacetone, which apparently corresponds to an energy gain on solvation of the diketo-form in dimethyl sulphoxide.

Reeves[114] and also Rogers and Burdett[118] compared the experimental keto–enol equilibrium constants for acetylacetone and acetoacetic ester with the values calculated taking into account the dielectric constant of the solvent[128]. For a number of solvents, in particular benzene and acetic acid, satisfactory agreement was obtained between theory and experiment. In other cases (pyrrole, triethylamine) there is a discrepancy between the calculations and experimental data owing to the specific interactions with solvent molecules[114]. The intermolecular hydrogen bond between pyrrole and the carbonyl groups of acetylacetone and acetoacetic ester stabilises the diketo-form. At the same time pyrrole does not interact significantly with the enolic form, as shown by the constancy of the chemical shift of the enolic proton when the concentration of the solution in pyrrole is altered[97,129].

Table 6. Enolisation and the screening of the enolic protons of α-substituted derivatives of acetoacetic ester $CH_3-CO-CHZ-COOC_2H_5$ (pure liquids)[95].

Z	Enol, %	τ_{OH}, p.p.m.
H	8	−2.17
CH_3	5	−2.63
C_2H_5	1	−2.73
n-C_3H_7	1	−2.80
iso-C_3H_7	1	−2.98
s-C_4H_9[a]	0.4	−3.10
s-C_5H_{11}	1.4	−3.30
CH_2—$CH=CH_2$	3	−2.70
CH_2—C_6H_5	22	−2.83
Br	5	−2.73
Cl	15	−2.28
F	15	—
CN	93 (75[b])	−3.45

a. See Ref. 102.
b. See Ref. 107.

Table 7. The content of the enol and the screening of the enolic protons of the esters of alicyclic oxo-, thiono-, and oxodithio-acids in carbon tetrachloride.

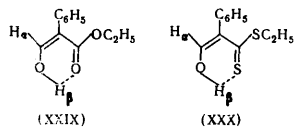
Type of ester	No. of methylene groups in ring	Enol, %	τ_{OH} (SH)
a	3	11.5 (21)[b]	−0.42
	4	85	−2.12
	5	31	−2.68
	6	64	−2.50
	7	38	−2.67
	8	70	−2.88
	9	13	−3.03
	10	7.5	−2.85
	13	7.0	−2.82
c	3	100	−2.51
	4	100	−2.57
	5	46	−2.48
	6	57	−2.33
d	3	99	3.83
	4	99	4.78
e	3	100	−4.01
	4	100	−5.37

a. See Ref. 108. b. See Ref. 98. c. See Ref. 109.
d. See Ref. 110. e. See Ref. 83.

In contrast to pyrrole, acetic acid, which is dimerised, does not form hydrogen bonds with acetylacetone[114] and has little effect on the position of its keto–enol equilibrium (Table 10).

b. Mode of Enolisation

NMR apparently provides a unique possibility of a quantitative estimation of the amounts of the two *cis*-enolic tautomeric forms (B) and (C). Aldo- and keto-esters and their thioanalogues enolise only at the carbonyl oxygen. This has been confirmed in a number of examples (XXIX–XXXIII). For (XXIX) and (XXX), the spin–spin coupling constants $J_{\alpha\beta}$ are characteristic of hydroxymethylene forms, amounting to 13.3 Hz [82] and 13.5 Hz [83] respectively, and are independent of temperature [87].



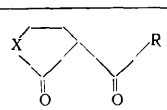
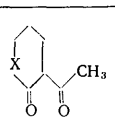
(XXIX) (XXX)

Table 8. Enolisation and the screening of the chelate protons of a number of esters of β-thiono-[110] and β-oxodithio-acids [83] in carbon tetrachloride.

Compound	Enol, %	τ_{OH}, p.p.m.	τ_{SH}, p.p.m.
$H_3C-CS-CH_2-COOC_2H_5$	96	—	2.70
$H_3C-CS-CH_2-COOC_4H_9$-n	94	—	2.65
$H_5C_2OOC-CH_2-CS-CH_2-COOC_2H_5$	96	—	2.75
$C_6H_5-CS-CH_2-COOC_2H_5$	97	—	2.05[a]
$C_6H_5-CS-CH_2-COSC_2H_5$	100[b]	—	2.02
$C_6H_5-CS-CH_2-CONHC_6H_5$	100[b]	—	—
$CH_3-CO-CH_2-CSSH$	100	−4.76	—
$CH_3-CO-CH_2-CSSCH_3$	94	−4.45	—
$CH_3-CO-CH_2-CSSC_2H_5$	94	−4.54	—
$C_6H_5CO-CH_2-CSSH$	100	−5.57	—
$C_6H_5CO-CH_2-CSSC_2H_5$	100	−4.99	—
$CH_3-CO-CH(CH_3)-CSSCH_3$	6	−5.73	—
$CH_3-CO-CH(C_6H_5)-CSSCH_3$	100	−5.67	—
$HCO-CH(C_6H_5)-CSSCH_3$	100	−4.63	—
$CH_3-CO-CH_2-CO-SC_2H_5$	30[c]	—	—

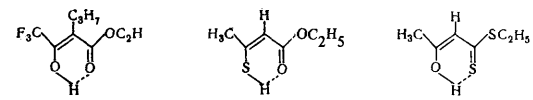
a. 1.65 in the pure liquid [98]. b. See Ref. 111.
c. Bromometric titration (pure liquid) [112].

Table 9. Enolisation and the screening of the enolic protons of a series of alicyclic β-dicarbonyl compounds with a heteroatom in the ring [113].

Compound	Medium	Enol, %	τ_{OH}
			
X=NCH$_3$; R=CH$_3$	DMSO	0	—
X=O; R=CH$_3$	$CDCl_3$	0	—
X=O; R=C$_3$H$_7$-n	$CDCl_3$	3	
	DMSO	3	−0.2
X=O; R=COOCH$_3$	$CDCl_3$	100	0.0
X=CH$_2$; R=CH$_3$[a]	CCl_4	60	−3.08
X=S; R=COOC$_2$H$_5$	$CDCl_3$	100	−2.17
			
X=NCH$_3$	DMSO	40.8	−5.18
X=CH$_2$[a]	CCl_4	100	−5.80
X=S	$CDCl_3$	74.6	−4.79
	DMSO	45.6	−4.83

a. See Ref. 88.

In the case of the ketoesters (XXXI)–(XXXIII) a similar conclusion was reached concerning the mode of enolisation, although the ^1H NMR data are more qualitative, since the spin–spin coupling constants are relatively low.



(XXXI) (XXXII) (XXXIII)

$J_{CF_3-\overset{\|}{C}-OH} = 2.0$ Hz [102] $J_{CH_3-\overset{\|}{C}-SH} = 1.0$ Hz [110] $J_{CH_3-\overset{\|}{C}-OH} = 0.66$ Hz [83]

Table 10. Thermodynamic functions for the enolisation of β-diketones R–CO–CHZ–CO–R′ (pure liquids).

R	Z	R	Temp. range, °C	Enol, % (33°C)	$-\Delta H$, kcal mole^{-1} (±0.2)	$-\Delta S$ (35°), kcal mole^{-1} deg^{-1} (±0.5)	Refs.
CH_3	H	CH_3	33—100	79.5	2.8[a]	6.4[a]	115 (114, 78, 100)
CH_3	H	C_2H_5	33—100	80.5	3.0	7.0	115
CH_3	H	iso-C_3H_7	33—150	89.0	3.2	6.4	115
CH_3	H	t-C_4H_9	33—150	93.5	3.9	7.4	115
iso-C_3H_7	H	iso-C_3H_7	33—150	94.0	3.7	6.6	115
iso-C_3H_7	H	t-C_4H_9	33—150	96.0	4.6	9.0	115
t-C_4H_9	H	t-C_4H_9	33—150	98.5	4.9	8.2	115
CH_3	CH_3	CH_3	(−11)—89	28	1.3	5.6	78 (100)
CH_3	$CH_2-CH=CH_2$	CH_3	25—125	42	2.1	7.3	100
CH_3	$CH_2-C_6H_5$	CH_3	38—170	46	2.5	8.4	100
CH_3	Cl	CH_3	33—80	92	5.9	14±1	78
C_6H_5	H	C_6H_5[b]	90—180	~100	3.2	3.4	100
C_6H_5	$COOC_2H_5$	C_6H_5[c]	—	56	10.1	40.0	116
Dimedone			20—85	—	2.0	—	117

a. In dimethyl sulphoxide ΔH and ΔS are 1.6 kcal mole^{-1} and 5.0 cal mole^{-1} deg^{-1}.
b. In carbon tetrachloride (0.4 M).
c. In chloroform.

Table 11. The content of the enolic form and chemical shifts of the acetylacetone and acetoacetic ester protons in various solvents [118].

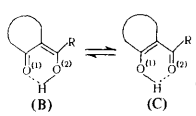
Solvent	Acetylacetone			Acetoacetic ester		
	Enol, %[a]	$\tau_\infty - \tau_0$, p.p.m.[b]		Enol, %[a]	$\tau_\infty - \tau_0$, p.p.m.[b]	
		=CH—	—OH		=CH—	—OH
$N(C_2H_5)_3$	100[c]	—	0	0[B]	—	—
C_6H_{14}	95	0.27	0.10	39.0	0.17	−0.05
CCl_4	96	0.20	0.35	28.0	0.15	0.10
$O(C_2H_5)_2$	95	0.12	0.35	22.0	0.10	−0.05
CS_2	94	0.22	0.27	20.0	0.15	0.12
C_6H_6	89	0.65	−0.68	16.0	0.15	−0.55
$CHCl_3$	87	0.03	0.33	7.5	0.05	0.13
Dioxan	82	0.03	0.63	11.0	0.03	0.03
C_2H_5OH (abs.)	82	−0.02	9.92[e]	10.0	0.03	0.02
Pyridine	82[d]	—	—	—	—	—
Pure liquid	81	0	0	7.5	0	0
Acetone	78[d]	—	—	—	—	—
CH_3OH	74	−0.05	10.42[e]	5.8	−0.02	0.02
CH_3COOH	67	0	0.53	1.9	0.03	0.07
CF_3COOH	66[r]	—	—	—	—	—
CH_3CN	62	−0.07	−0.17	4.9	0	0.02
CH_3SOCH_3	62	−0.13	1.13	2.2	−0.08	0.10

a. In 0.1 M solutions.
b. τ_∞ is the chemical shift extrapolated to infinite dilutions and τ_0 the chemical shift for the pure liquid.
c. Data from Refs. 114 and 119.
d. Data from Ref. 89.
e. Chemical shift of the overall signal of the enolic protons and the hydroxyl protons of the alcohol.

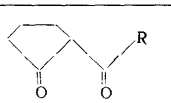
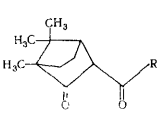
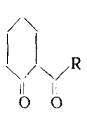
In contrast to aldoesters, β-aldoketones exist in both *cis*-enolic forms (B) and (C). Table 1 presents data on the mode of enolisation in cyclic α-formylketones determined from the chemical shift of the aldehyde (hydroxymethylene) proton; these agree with the spin–spin coupling constants ($J_{=CH-OH}$) [19]. According to Garbisch [130], the differences in the mode of enolisation are associated mainly with the conformations of the rings and their strain. The predominance of the hydroxymethylene form (B) in five-membered rings and of form (C) in six-membered rings is consistent with quantum-chemical calculations indicating that exocyclic carbon–carbon double bonds are energetically favourable for five-membered rings [131]. The ^{1}H NMR data for α-formylcyclohexanone and 3-formylcamphor are also satisfactorily consistent with the results obtained from ^{17}O NMR spectra [22].

Deutsch and Deutsch [87], who investigated the same compounds as Gabrisch, believed erroneously that rapid (B) ⇌ (C) exchange should lead to the disappearance of the multiplet structure of the hydroxymethylene (aldehyde) and enolic proton signals (as happens in intermolecular exchange). Therefore the very fact that these signals are split was incorrectly interpreted as evidence for the existence of the hydroxymethylene form only. Their work [87] was criticised in detail in a later paper by Garbisch [132].

Table 12. The mode of enolisation and ^{17}O screening (relative to H_2O) in a series of alicyclic β-diketones and β-ketoaldehydes in benzene [22].



(B) (C)

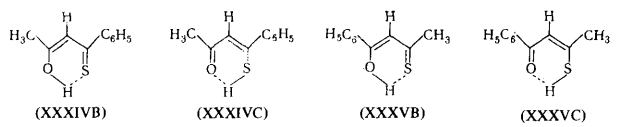
Compound	$\delta_0^{(1)}$, p.p.m.	$\delta_0^{(2)}$, p.p.m.	$\frac{[B]}{[B]+[C]}$, %
 R = CH_3[a]	354	169	70
R = C_6H_5	395	121	80
 R = H	430	88	87
R = CH_3	408	108	83
 R = H	205	360	33
R = CH_3	175	359	30
R = C_6H_5	231	295	43

a. The ^{17}O signal of the diketo-form is observed ($\delta_0^{(1)} \simeq \delta_0^{(2)} \simeq 540$ p.p.m.).

Forsen and Nilsson [86] observed a temperature variation of the $J_{=CH-OH}$ constant for α-phenylacetoacetaldehyde. Possibly it reflects a shift in the (B) ⇌ (C) equilibrium.

Gorodetsky et al [22] succeeded in estimating the contents of the two *cis*-enolic forms for a number of alicyclic β-diketones (Table 12) and benzoylacetone from ^{17}O NMR spectra. Table 12 shows that in β-diketones the effect of ring size on the mode of enolisation is similar to that found for aldoketones. Replacement of a methyl group in the side chain by a phenyl group leads to an increase in the amount of the form with exocyclic double bonds. The stabilisation of this form by the benzene ring owing to the increase in the length of the conjugated chain was predicted by quantum-mechanical calculation [133]. Probably for this reason the enolisation of benzoylacetone (V) at the carbonyl group adjacent to the benzene ring is preferred (about 56%) [22]. These quantitative data were contradicted in a later study by Sardella et al. [94], who did not observe spin–spin coupling between the methyl and vinyl protons of benzoylacetones and thereby concluded that more than 90% is present as the form with an enolised benzoyl group. The resolution of this contradiction requires additional studies, but we believe the data of Gorodetsky et al. [22] to be more convincing.

The problem of the mode of enolisation of thionoketones is interesting. Klose et al. [125] observed the spin–spin splitting of the enolic proton signal by the protons of the methyl group of thiobenzoylacetone (XXXIV) and concluded that thionoketones are enolised at the carbonyl group.



(XXXIVB) (XXXIVC) (XXXVB) (XXXVC)

$J_{CH_3-\overset{\|}{C}-OH} = 0{,}32$ Hz $J_{CH_3-\overset{\|}{C}-SH} = 0{,}20$ Hz

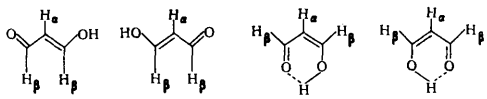
However, Duus and Lawesson [110] observed a splitting of the signal due to the chelate proton in benzoylthioacetone (XXXV) [110], and in accordance with infrared spectroscopic data, suggested that thionoketones are enolised at the thiono-group. The presence of both forms in comparable amounts is quite likely. The sharp increase of the screening of the chelate proton of thionoketones with increase of temperature [110,125] is explained by the shift of the equilibrium towards the thienol form¶ [125] or the dissociation of the intramolecular hydrogen bond [126].

One can postulate a parallel variation of the capacity for enolisation of the RCO–group in aldoketones and diketones, on the one hand, and in the corresponding ketoesters, on the other, with the nature of the substituent R. Indeed a correspondence is observed between the content of the enol in ketoesters (Table 7) and the fraction of the chelate aldo-form (C) in the corresponding aldoketones (Table 1). Furthermore, the preferential enolisation of the benzoyl group of benzoylacetone is consistent with the greater ease of enolisation of the benzoylacetic ester compared with acetoacetic ester (Table 3). Consequently the more pronounced enolisation of ring-substituted benzoylacetic esters with increasing electronegativity of the substituent [93,99] (Table 4) should correspond to an increase of the content of the chelate form with an enolised benzoyl group in the analogous benzoylacetones. This is consistent with the results of a study [93] based on an analysis of the chemical shifts of enolic protons.

¶ The signal of the chelate proton of the thienol form is located in higher fields (Table 8).

c. *trans*-Enolisation

On the basis of the $J_{\alpha\beta} = 9.69$ Hz constant, Bothner-By and Harris[84] concluded that malonodialdehyde exists in chloroform mainly in the *trans*-transoid form (XXXVI, D and E).



(XXXVID) (XXXVIE) (XXXVIB) (XXXVIC)

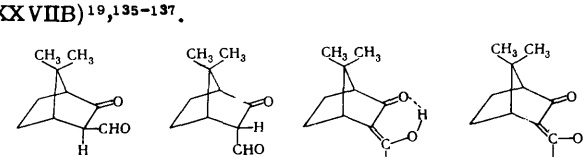
However, according to the data of Shapet'ko et al.[85], this constant is 4.2 Hz in chloroform and acetone and therefore the authors attributed the *cis*-cisoid structure (XXXVI, B and C) to malonodialdehyde. This structure is also indicated by the marked descreening of the enolic proton (about 0 p.p.m.). George and Mansell[79] confirmed Shapet'ko's data ($J_{\alpha\beta} = 3.4-3.8$ Hz in carbon tetrachloride, chloroform, and methylene dichloride), i.e. the structure (XXXVI, B and C). They explained the results of Bothner-By and Harris[84] by the presence of polar impurities in chloroform.

In aqueous solution the enolic forms of malonodialdehyde ($J_{\alpha\beta} = 10.3$ Hz) and also of α-formylacetone ($J_{\alpha\beta} = 9.1$ Hz) have the *trans*-transoid structure according to George and Mansell[79]. This behaviour can evidently be explained by competition between intramolecular hydrogen bonding and strong intermolecular hydrogen bonds with water molecules.

Freshly prepared solutions of α-phenylformylacetic esters in chloroform contain the *trans*-enolic form but after a time are fully converted into the *cis*-enolic and aldo-forms[84].

In 1967 a Japanese group[103] reported the presence of large amounts (up to 50%) of the *trans*-enolic forms of a number of α-alkylacetylacetones in carbon tetrachloride. This conclusion contradicts other data[101,102,134] (^{1}H NMR and bromometric titration), which show that the enolisation of the above compounds is insignificant (about 1% or less) in various media, the enolic tautomer being in the *cis*-form. Possibly the Japanese workers were not dealing with the *trans*-enols but with the enol esters[101].

The *trans*-enolic form of 3-formylcamphor (XXXVIID) was observed in various solvents in slow equilibrium with the aldo-form (XXXVIIA) and the *cis*-enolic form (XXXVIIB)[19,135-137].



(XXXVIIA) (XXXVIIB) (XXXVIID)

In carbon tetrachloride the ratio of the concentrations of the *trans*- and *cis*-forms of the enol D/B increases according to ^{1}H NMR data from 5/95 in 10% solution to 31/69 in 26% solution[19]. The addition of dimethyl sulphoxide to carbon tetrachloride sharply increases the content of the *trans*-enolic form[19,135] (D/B = 78/22 for 14% solution in carbon tetrachloride with 8% of dimethyl sulphoxide). In 10% solution in ether, D/B = 55/45.[136] The increased content of the *trans*-enolic form of 3-formylcamphor is probably due to a competition between intramolecular and intermolecular hydrogen bonding.

The fact that in non-aqueous media the *trans*-enolic form has so far been detected only in 3-formylcamphor (among a large number of compounds investigated) may be tentatively accounted for by the weakness of intramolecular hydrogen bonding in this compound (see below).

On the basis of a private communication by Duus et al., Wamhoff et al.[113] state that α-thioacetyl-γ-butyrolactone contains 37% of the *trans*-enolic form in carbon tetrachloride.

d. Intramolecular Hydrogen Bonds in β-Dicarbonyl Compounds

Intramolecular hydrogen bonding determines the stability of the *cis*-enolic form and with other factors, the position of the keto–enol equilibrium. Therefore here we shall examine the factors which influence the chemical shift of the chelate enolic proton (τ_{OH}). The chemical shift may be a quantitative characteristic of the strength of intramolecular hydrogen bonding in a series of similar compounds. The stronger the intramolecular hydrogen bond, the lower is the value of τ_{OH}.[5] On the other hand, τ_{OH} contains, in principle, information about the enol–enol equilibrium.

The weak dependence of the chemical shift of the ^{1}H NMR signal of the *cis*-enolic proton on temperature[78,102,126] and on the medium (Table 11)[90,138] and also the spin–spin splitting of this signal observed in many cases indicate the stability of the chelate ring with an intramolecular hydrogen bond.

Tables 2, 3, 5, and 6 show that τ_{OH} decreases with increasing size of both the terminal groups and (to an even greater extent) the size of the α-substituent (Z). This finding can be explained by the repulsion of the groups, as results of which the chelate ring contracts, the oxygen atoms come closer together, and the intramolecular hydrogen bond is strengthened[91,95,139]. On the other hand, steric effects account for the shift of the chelate proton signal of α-formyl, α-acetyl, and α-ethoxycarbonyl-pentanones and particularly α-formylcamphor towards higher fields by 2–3.5 p.p.m. relative to the corresponding acyclic compounds (Tables 1, 7, and 9). With increase of the valence angles at the unsaturated carbon atoms in the rings of the above compounds to 107–111°, the intramolecular hydrogen bond becomes weakened owing to the increased distance between the oxygen atoms[19,108].

The more pronounced descreening of the enolic proton in diketones compared with aldoketones and particularly compared with ketoesters is associated with the increase of the electronegativity of substituents in the series Alk < H < OAlk.

In β-ketoesters τ_{OH} depends only slightly on the electronegativity of the terminal substituent (Table 3). This effect is almost absent from *para*-substituted benzoylacetic esters (Table 4).

In β-diketones the electronic influence of the terminal substituent is much more marked. Electronegative substituents reduce the strength of the intramolecular hydrogen bond (Table 2) evidently due to the decreased electron density at the carbonyl oxygen[91]. The benzene ring supplies electrons to the chelate ring and stabilises the intramolecular hydrogen bond, provided that it is conjugated† with the chelate ring. When the mesityl

† The coplanarity of the benzene and chelate rings is confirmed by the descreening of the *ortho*-protons of the ring on the side of the carbonyl group[90].

group is displaced from conjugation, it does not have a significant influence on τ_{OH} (Table 2).

In the majority of compounds the effect of the electronegativity of the α-substituent (Z) on τ_{OH} is masked by steric effects. But if the dimensions of the substituents are similar, ^{1}H NMR data indicate that the screening of the enolic proton decreases with increasing electronegativity in both ketoesters and diketones (cf. Z = Cl and Z = CN, Tables 5 and 6).

The replacement of the −COOAlk group by −CSSAlk in aldo- and keto-esters leads to a marked shift of the enolic chelate proton signal towards lower fields (by 2−3 p.p.m.) (Table 8). On the other hand, the replacement of the acyl group of ketoesters by the thioacyl group causes a sharp shift (by 4−5 p.p.m.) of the resonance of the chelate proton towards higher fields. In β-thionoketones the chelate proton is more highly screened than in the corresponding diketones.

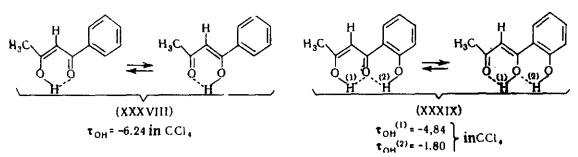
e. Effect of the Enol−Enol Equilibrium on the Chemical Shift of the Enolic Proton

As a result of the migration of the proton of the intramolecular hydrogen bond between the donor atoms, an average chemical shift of the two *cis*-enolic forms (B) and (C) is observed. The marked dependence of τ_{OH} for β-diketones (Y = Alk) on the nature of the terminal substituent X is largely due to changes in electron density at the oxygen atom of the adjacent carbonyl group in the tautomer (B).

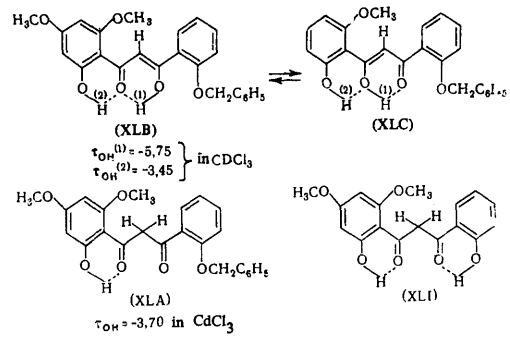
In β-ketoesters (Y = OAlk) the form (B) is absent and the change in electron density at the remote carbonyl group of the tautomer (C) is insignificant. Hence the weak dependence of τ_{OH} on the electronegativity of the substituent in β-ketoesters becomes understandable[93]. The closer the values of τ_{OH} for two chelate forms, the weaker is the influence of the displacement of the intrachelate equilibrium on the observed chemical shift of the enolic proton.

f. Compounds with two Intramolecular Hydrogen Bonds

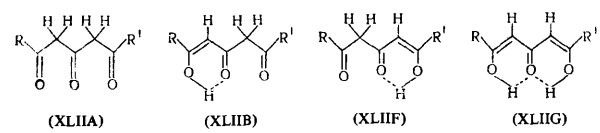
The formation of a second intramolecular hydrogen bond with a chelate oxygen atom reduces the strength of the first intramolecular hydrogen bond. This conclusion was reached after comparing the values of τ_{OH} for compounds (XXXVIII) and (XXXIX) and also for analogous toluene and naphthalene derivatives[140].



Possibly the effect of the second intramolecular hydrogen bond (with the phenolic proton) is one cause of the low content of the enolic form (about 30%) in compound (XL) and other similar compounds[141] compared with dibenzoylmethanes without a hydroxy-group (Table 2). Indeed, in compound (XLI), where both carbonyl groups are stabilised by intramolecular hydrogen bonds, there is no appreciable enolisation[141]. Wagner et al.[141] suggest that, of the two possible enolic forms of (XL), the form (XLB) where the free carbonyl group is enolised, is the more stable:



In the triketones (XLII, R, R′ = CH_3 or C_6H_4X), the contents of the tautomers (A), (B), (F), and (G), (3, 40, 18, and 39% respectively for H = C_6H_5 and R′ = CH_3 in $CDCl_3$) have been determined[99,142]. The low content of the form (G), i.e. the reduced capacity for enolisation of the acetyl and benzoyl groups relative to the corresponding diketones, may be associated with the lower strength of the two intramolecular hydrogen bonds.



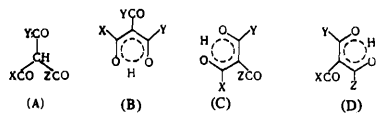
The greater tendency of the benzoyl group towards enolisation compared with the acetyl group is noteworthy.

5. TRIACYLMETHANES AND SIMILAR COMPOUNDS

In general three enolic forms (external tautomers[88]), differing in the group outside the chelate rings (B, C, D), are possible for acyclic tricarbonyl compounds related to triacylmethanes (Table 13). In cyclic tricarbonyl compounds there may be two non-equivalent chelate forms (Table 14). Usually tricarbonyl compounds do not contain the triketo-form (A) in an appreciable amount. However, the compounds with even a single large substituent, such as t-butyl, are not enolised at all[143] and certain acyldibenzoylmethanes and tricarbonyl compounds with ester groups are only partly enolised (Table 13). The content of the enolic forms of these compounds decreases in polar solvents[116]. The interconversions of the external tautomers, which require the dissociation of intramolecular hydrogen bonds, are slow under the usual conditions and the observed ^{1}H NMR spectrum contains the individual signals of the tautomers. The rate of exchange increases sharply in the presence of bases[88,106].

A stronger intramolecular hydrogen bond is characteristic of tricarbonyl compounds compared with the corresponding dicarbonyl compounds (lower values of τ_{OH} and of the vibration frequencies of the C=O and O−H groups in the infrared spectra)[88,148]. The high enthalpy of enolisation of dibenzoylethoxycarbonylmethane (Table 10) and the slow deuterium exchange involving the chelate protons in 2-acetyldimedone[5] are also consistent with the high stability of the intramolecular hydrogen bonds in tricarbonyl compounds. The high stability of the chelate enolic forms of tricarbonyl compounds can be understood by regarding them as β-dicarbonyl compounds with an

Table 13. Tautomeric composition and the screening of the enolic protons of acyclic tricarbonyl compounds.

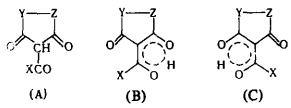


(A) (B) (C) (D)

Compound X	Compound Y	Compound Z	Medium	Tautomers, % A	B	C	Γ	τ_{OH}, p.p.m. B	C	Γ	Refs.
CH_3	CH_3	CH_3	$CDCl_3$	0	33	33	33	−7.41	−7.41	−7.41	105
CH_3	C_6H_5	CH_3	$CDCl_3$	0	100	0	0	−7.05	—	—	143
C_3H_7	C_6H_5	C_3H_7	$CDCl_3$	0	100	0	0	−7.20	—	—	143
C_4H_9	C_6H_5	C_4H_9	$CDCl_3$	0	100	0	0	−4.45	—	—	143
C_3H_7	$OCH_3C_6H_4$	C_3H_7	$CDCl_3$	0	100	0	0	−7.00	—	—	143
C_3H_7	$NO_2C_6H_4$	C_3H_7	$CDCl_3$	0	100	0	0	−7.35	—	—	143
CH_3	C_6H_5	C_6H_5	$CDCl_3$	0	50	50	0	−7.29	−7.29	—	144, 145
C_3H_7	C_6H_5	C_6H_5	$CDCl_3$	>5	<50	<50	0	−7.35	−7.35	—	144, 145
CH_3	$NO_2C_6H_4$	C_6H_5	$CDCl_3$	0	50	50	0	−7.42	−7.05	—	144, 145
C_3H_7	$NO_2C_6H_4$	C_6H_5	$CDCl_3$	0	50	50	0	−7.60	−7.30	—	144, 145
CH_3	$-CH=CH-C_6H_5$	CH_3	CCl_4	0	66	17	17	−7.30	−7.40	−7.40	106
CH_3	H	CH_3	CCl_4	0	80	10	10	−8.30	−7.10	−7.10	86
CH_3	OC_2H_5	H	CCl_4	0	90	10	0	−7.10	−4.40	—	86
CH_3	OCH_3	CH_3	CCl_4	0	100	0	0	−8.62	—	—	106
CH_3	OC_2H_5	CH_3	$CDCl_3$	2	96	1	1	−8.20	—	—	116
CH_3	OC_2H_5	CH_3	DMSO	7	90	1.5	1.5	−7.90	—	—	116
CH_3	OC_2H_5	C_6H_5	$CDCl_3$	16	54	30	0	−7.10	−3.20	—	116, 144, 145
CH_3	OC_2H_5	C_6H_5	DMSO	40	—	60	—	—	—	—	116
C_6H_5	OC_2H_5	C_6H_5	$CDCl_3$	44	13	21.5	21.5	−7.5	−3.7	−3.7	116
C_6H_5	OC_2H_5	C_6H_5	DMSO	94	0	3	3	—	—	—	116
C_6H_5	OC_2H_5	C_6H_5	CCl_4	25	15	30	30	−7.90	−3.7	−3.7	117
CH_3	OC_2H_5	OC_2H_5	CCl_4	43	28.5	28.5	0	—	—	—	110
C_6H_5	OC_2H_5	OC_2H_5	pure liquid	93	3.5	3.5	0	−3.51	−3.51	—	146
t-C_4H_9	OC_2H_5	OC_2H_5	ditto	100	0	0	0	—	—	—	146

a. The representation of the chelate forms employed here implies the possibility of the migration of the proton between the oxygen atoms, i.e. rapid intrachelate tautomerism.

Table 14. Tautomeric composition[a] and the screening of the enolic protons for cyclic tricarbonyl compounds.



(A) (B) (C)

Compound X	Compound Y–Z	Medium	Tautomers, % B	C	τ_{OH}, p.p.m. B	C	Refs.
CH_3	CH=CH	CCl_4	50	50	−2.10	−2.10	88
CH_3	CH=CCl	CCl_4	69	31	−(−1.83)[b]		88
CH_3	$CH=CCH_3$	CCl_4	62	38	−(−2.19)		88
CH_3	$CH_2-C(CH_3)_2$	CCl_4	60	40	−(−4.52)		88
CH_3	$(CH_2)_2$	CCl_4	50	50	−4.75	−4.75	88
CH_3	$(CH_2)_3$	CCl_4	50	50	−8.03	−8.03	88
CH_3	$(CH_2)_4$	CCl_4	50	50	−7.87	−7.87	88
H	$(CH_2)_2$	$CDCl_3$	50	50	−2.32	−2.32	147
H	$CH_2-C(CH_3)_2-CH_2$	CCl_4	50	50	−5.60	−5.60	86
CH_3	$CH_2-C(CH_3)_2-CH_2$	CCl_4	50	50	−8.06	−8.06	88
NH_2	$CH_2-C(CH_3)_2-CH_2$	$CDCl_3$	50	50	−7.78	−7.78	120
CH_3	$C(CH_3)_2-C(OCH_3)=CH$	$CDCl_3$	50	50	—	—	16, 105
iso-C_3H_7	$C(CH_3)_2-C(OCH_3)=CCH_3$	$CDCl_3$	65	35	−9.40	−8.70	16
CH_3	$CH=C(CH_3)-O$	$CDCl_3$	0	100	—	−7.02	148

a. The triketo-form (A) was not detected.
b. Overall signal. The signals due to the protons at the carbon atoms are observed separately.

electronegative α-substituent (–COX). The dependence of τ_{OH} for di- and tri-carbonyl compounds on the substituent and ring size is analogous.

Many studies have been made to determine the mode of chelation of tricarbonyl compounds. In a number of cases the problem has been solved (Tables 13 and 14) despite the difficulty associated with the similarity of the chemical shifts of the acyl groups in the chelate and outside it‡. Nonhebel[143] showed by infrared and ^1H NMR spectroscopy that in diacetylaroylmethanes the aryl group is not incorporated in the chelate and in acetyldiaroylmethanes the acetyl group must be involved in the formation of the chelate (Table 13). The data in this table also show that the ester groups are preferentially located outside the enolic chelate ring.

The contents of the external tautomers of a number of complex tricarbonyl compounds (mainly natural compounds) have been investigated[16,120,149,150]. The intrachelate tautomerism of tricarbonyl compounds has not been specially investigated, but in a number of studies it has been discussed on the basis of indirect data[86,147,150].

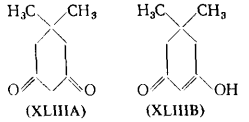
6. CYCLIC β-DIKETONES

In contrast to acyclic and alicyclic β-diketones, in the enolic forms of the cyclic β-diketones considered in this section intramolecular hydrogen bonds stabilising the enolic form cannot be formed owing to steric factors when the ring is not unduly large. Therefore in dilute solutions in non-polar media the contents of the enolic forms of cyclohexane-1,3-dione and dimedone (XLIII) are low. The percentage of the enolic form of the cyclic ketone increases sharply with concentration (in contrast to acyclic β-diketones). With increased concentration of dimedone in chloroform from 0.020 to 0.094 M, the content of its enolic form increases from 5 to 28%.[151] Cyclohexane-1,3-dione is enolised to a greater extent than dimedone, but the form of its concentration dependence is the same for both compounds. A similar variation

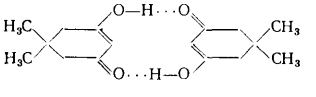
‡ 7.89 and 7.72 p.p.m. for triacetylmethane[143].

of the tautomeric composition of the compounds with concentration is observed also in acetonitrile, despite its high polarity, probably due to the relatively weak proton-acceptor properties of acetonitrile. In proton-accepting solvents the enolic form predominates at all concentrations[16,152]. At higher temperatures, the content of the diketo-form of dimedone and cyclohexane-1,3-dione increases[117]. The dependence of the degree of enolisation on concentration, solvent, and temperature can be explained by the formation of intermolecular hydrogen bonds by the enolic forms with one another and with the proton-accepting solvent molecules.

The ^{1}H NMR spectrum of dimedone contains the signals of both the keto- and enolic forms[72]. The individual signals of the non-equivalent methylene groups of the enolic form§ indicate a low rate of interconversion (the lifetime exceeds one second) of the two equivalent enolic forms of the type (XLIIIB), in contrast to the intrachelate enol-enol transformation of acyclic β-diketones (lifetime $< 10^{-4}$ s).


(XLIIIA)

(XLIIIB)

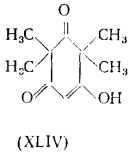

(XLIIIC)

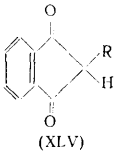
Cyr and Reeves[117] suggested that the tautomerism of dimedone and cyclohexane-1,3-dione in non-polar media can be described by the equilibrium ketone (A) ⇌ monomeric enol (B) ⇌ dimeric enol (B′).

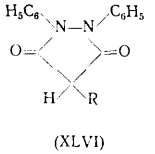
However, Yoge and Mazur[151] demonstrated the presence also of polymeric enolic forms, the fraction of which increases with concentration.

In contrast to β-diketones with intramolecular hydrogen bonds, the enolic proton signal of cyclic β-diketones is significantly displaced towards higher fields on dilution with a non-polar solvent (for dimedone, the values of τ_{OH} extrapolated to high and low concentrations are +0.34 and −2.32 p.p.m. respectively[117]). The observed enolic proton signal is the common signal of the monomeric and all the polymeric enolic forms in view of their rapid interconversion and the increase of τ_{OH} reflects the increase of the relative content of the monomeric form (B) with the free OH group.

^{1}H NMR data[151] indicate a higher rate of inversion of the ring of the diketo-form of dimedone compared with the ring of the enolic form. Bick and Horn[16] showed that the content of the enolic form of syncarpic acid (XLIV) is insignificant in chloroform but increases sharply in the presence of small amounts of water and dimethyl sulphoxide. In acetone the form (XLIV) predominates. The rate of the keto-enol transformation increases sharply (until the merging of the corresponding ^{1}H NMR signals) in the presence of traces of bases.


(XLIV)

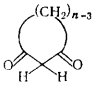

(XLV)

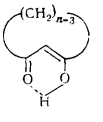

(XLVI)

§ The chemical shifts of the methylene group protons of the enol are close to those of the methyl ether of dimedone[153,154].

The ^{1}H NMR data for five-membered cyclic β-diketones are restricted to indanedione (XLV, R = H) and its 2-phenyl derivative (XLV, R = C_6H_5).[95] The spectra did not show the signals of the enolic form in chloroform and dioxan, in agreement with the general hypotheses concerning the tautomerism of indanediones[155,156]. The enolic form was not observed in any of the 4-alkyl-3,5-dioxo-1,2-diphenylpyrazolidines (XLVI)[157].

There are no literature data on the tautomerism of β-diketones containing between 8 and 10 atoms in the ring¶. For steric reasons, the chelate enolic forms with intramolecular hydrogen bonds are impossible in these compounds. β-Diketones with a large number of ring atoms were investigated by Kirrman and Wakselman[158]. The chelate enolic forms (XLVIIB) of these compounds have been detected; their content increases with ring size (20% for $n = 11$, 60% for $n = 12$, and more than 95% for $n = 14$ and 17 in carbon tetrachloride). The enolic proton signals are close (5 p.p.m.) to the values of τ typical for acyclic β-diketones.


(XLVIIA)


(XLVIIB)

¶ Cyclobutane-1,3-dione[159] and cycloheptane-1,3-dione[160] are weakly enolised.

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Primary Photoionisation Processes and Ion-Molecule Reactions in Organic Compounds

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This review deals with studies on primary photoionisation and molecular decomposition processes and ion-molecule reactions in the gas phase. Problems concerning the nature of the electronic and vibrational states arising on photoionisation and their role in unimolecular and bimolecular reactions of organic compounds are discussed.
Various pathways for the formation of secondary products in ion-molecule reactions have been determined. Data are presented on the energy relations of ion-molecule reactions and the proton affinities of molecules.
The bibliography includes 69 references.

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I. INTRODUCTION

During recent years a new field has developed in the photochemistry of organic compounds—the photochemistry of gaseous ions, considering the elementary photoionisation processes and ion–molecule reactions (IMR) involving the ions formed on photoionisation. The development and application of the mass-spectrometric photoionisation method[1-3] yielded information about the excited and electronic states of radical-cations and the role of these states in the unimolecular decomposition reactions of the radical-cations into cations and radicals. The use of the appearance potentials of fragment ions made it possible to determine the heats of formation of cations of different structures and to refine the heats of formation obtained earlier by the electron impact method.

The data thus obtained on the electronic states and heats of formation of ions made it possible to consider the problem of the mechanisms and the pathways of ion–molecule reactions, which play an important role in high-energy chemistry and in the two-quantum photochemistry of organic compounds[4]. In the first place this concerns the elucidation of the role of the excitation of primary ions in ion–molecule reactions with the aim of investigating the mechanism by which the energy of the colliding species is redistributed. In the second place, for the study of the mechanism of ion–molecule reactions, it is important to know the different pathways for the formation of secondary ions and radicals both by hydrogen atom transfer from various groups of the molecule to the radical-cation and as a result of the involvement in the reactions of primary fragment ions. In the third place the elucidation of the way in which molecular properties such as basicity and polarisability influence the nature of ion–molecule reactions is very important.

In the present review these problems are considered in the discussion of studies on photoionisation and ion–molecule reactions occurring in the photoionisation of simple molecules and organic compounds—saturated and unsaturated hydrocarbons, aromatic hydrocarbons, aromatic compounds with heteroatoms, and aromatic hydrocarbons.

The studies on ion–molecule reactions by the electron impact methods have been reviewed[5-7]. The review of Tal'rose and Karachevtsev[5] deals with the study of ion–molecule reactions by the so called method of "internal" ionisation of molecules by electrons (the method of pulse withdrawal of ions). This method was first developed and applied by Tal'rose and Frankevich to measure the rate constants for ion–molecule reactions[8,9] and also to determine the proton affinities of molecules[10,11]. In subsequent studies the method of pulse withdrawal of ions was successfully employed in investigations of the mechanism of ion–molecule reactions involving thermal ions.

Important information about ion–molecule reactions was obtained by applying methods which permit the determination of the kinetic energies of ions produced in the reactions. The deflecting field method was used to determine the average kinetic energies of secondary ions and yielded information about the redistribution of the energy of the colliding species in ion–molecule reactions among the internal and translational degrees of freedom[12,13]. Measurement of the product energies for ion–molecule reactions by determining the changes in the momenta of secondary ions compared with the momentum which the primary ion receives when the molecule is ionised by an electron yielded data on the mechanism of ion–molecule reactions[14].

We may note that other aspects of ion–molecule reactions have also been elucidated[6,7,15]: the dependence of the cross-sections on the kinetic energy of the ions, angular distribution of products, etc.

Ion–molecule reactions in simple systems have been examined theoretically in studies on bimolecular gas-phase reactions[16,17]. It has been shown that ion–molecule reactions proceed via two pathways[16], namely via an intermediate complex mechanism and via a direct mechanism involving the "scission" of an ion from the incident species or the "capture" of a neutral species by the incident ion.

II. PHOTOIONISATION AND ION–MOLECULE REACTIONS IN SIMPLE MOLECULAR AND NOBLE GASES

1. Hydrogen

The ion–molecule reactions which occur on photoionisation of hydrogen were first investigated by Chupka et al.[3], who showed that the formation of the secondary H_3^+ ions involves the participation both of molecular hydrogen ions H_2^+ and excited hydrogen atoms. The primary molecular hydrogen ions H_2^+ were obtained in various excited vibrational states when hydrogen molecules were acted upon by monochromatic radiation (the energy spread was 0.002–0.05 eV) (Fig. 1):

$$H_2\,(X^1\Sigma_g^+,\ v''=0)+h\nu \rightarrow H_2^+\,(^2\Sigma_g,\ v'\geqslant 0)+e\,. \qquad (1)$$

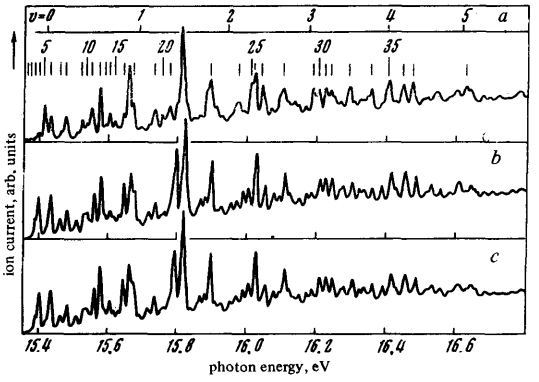

Figure 1. Appearance curves for H_2^+ and H_3^+ ions recorded with a resolution of 0.4 Å: *a*) H_2^+ from normal hydrogen; *b*) H_2^+ from parahydrogen; *c*) H_3^+ from parahydrogen.

Hydrogen atoms in the excited metastable state 2*S* were formed as a result of the predissociation of hydrogen molecules in the excited electronic state $D^1\Pi_u$:

$$H_2\,(X^1\Sigma_g^+,\ v''=0)+h\nu \rightarrow H_2\,(D^1\Pi_u,\ v'\geqslant 3) \rightarrow H_2\,(B^1\Sigma_u^+) \rightarrow H\,(1S)+H\,(2S)\,. \qquad (2)$$

This predissociation region of hydrogen molecules converges to a threshold of 14.66 eV. At the predissociation threshold the hydrogen atoms in the 2*S* state are formed with thermal kinetic energy, while for photon energies of 14.77 and 15.01 eV the hydrogen atoms in the 2*S* state are mainly produced as a result of the deactivation of hydrogen molecules in the excited vibrational states $v = 3$ and $v = 4$ respectively. The kinetic energies of the metastable hydrogen atoms corresponding to photon energies of 14.77 and 15.01 eV have been shown to be[18] 0.18 and 0.27 eV.

The cross-section of an ion–molecule reaction involving molecular hydrogen ions in the ground and excited vibrational states (Fig. 2),

$$H_2^+\,(^2\Sigma_g,\ v'\geqslant 0)+H_2\,(X^1\Sigma_g^+,\ v''=0) \rightarrow H_3^+ + H\,(1S)\,, \qquad (3)$$

decreases by 15–20% with increase of photon energy from the hydrogen ionisation potential (15.425 eV) to 16.6 eV. A decrease of the cross-section of reaction (3) with increasing vibrational excitation of the molecular ions H_2^+, i.e. with increase of the vibrational quantum number v from 0 to 5 is observed for kinetic energies of the primary ions less than 2 eV (laboratory system).

Studies on ion–molecule reactions in hydrogen on a double mass-spectrometer[19] showed that H_3^+ ions are formed via two pathways: both via proton and hydrogen atom transfer. With increase of the kinetic energy of molecular hydrogen ions from 1 eV upwards, the contribution of the process involving hydrogen atom transfer to the formation of secondary H_3^+ ions increases. For these kinetic energies of the molecular ions, both processes involve a direct mechanism, since their cross-sections are independent of the vibrational excitation energy of the molecular ions and the cross-section of the proton transfer process actually increases with increasing vibrational excitation of H_2^+ to 2 eV. For kinetic energies close to thermal energies, the proton transfer process contributes significantly to the formation of H_3^+ ions.

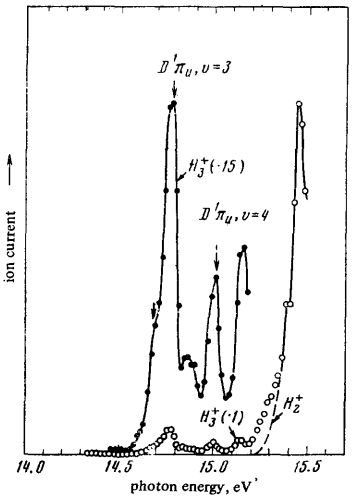

Figure 2. Appearance curves for H_2^+ and H_3^+ ions in the chemi-ionisation region recorded with a resolution of 2.5 Å. The arrow indicates the dissociation threshold of the hydrogen molecule (14.66 eV).

Fig. 2 shows that, in the range of photon energies below the hydrogen ionisation potential, the formation of H_3^+ ions involves the reaction of metastable hydrogen atoms with hydrogen molecules:

$$H\,(2S)+H_2\,(X^1\Sigma_g^+,\ v''=0) \rightarrow H_3^+ + e\,. \qquad (4)$$

Reaction (4) is exothermic, since at the predissociation threshold of the hydrogen molecule (14.66 eV) it involves metastable hydrogen atoms with thermal velocities. This finding serves as a basis for the determination of the heat of formation of H_3^+ ions:

$$\Delta H_f[H_3^+] \leqslant \Delta H_f[H(2S)] = 12.455\ \text{eV},$$

which corresponds to the lower limit of the proton affinity of the hydrogen molecule (3.396 eV).

On passing to photon energies of 14.77 and 15.01 eV, for which metastable hydrogen atoms are formed with an excess kinetic energy, the cross-section of reaction (4) has been shown[18] to decrease as v^{-n}, where v is the

velocity of the hydrogen atom and $n = 2-3$. In the range of photon energies between 15.20 eV and the hydrogen ionisation potential (15.425 eV), the observed increase of the yield of secondary H_3^+ ions must be attributed to reactions involving electronically excited hydrogen molecules:

$$H_2^* + H_2 (X^1\Sigma_g^+, v'' = 0) \rightarrow H_3^+ + H^- , \quad (5)$$

$$H_2^* + H_2 (X^1\Sigma_g^+, v'' = 0) \rightarrow H_3^+ + H(1S) + e . \quad (6)$$

It is important to note here that the contribution of reaction (4) to the formation of H_3^+ ions in this range of energies is insignificant for the reason indicated above. It has been shown[20] that highly excited long-lived states of the hydrogen molecule with a principal quantum number $n > 5$ play a significant role in reactions (5) and (6). The energies of such states lie in the region 0.1–0.2 eV below the ionisation potential of the hydrogen molecule.

2. Hydrogen and Noble Gases

The studies on the ion–molecule reactions observed in the ionisation of hydrogen molecules and noble gases by electron impact have dealt mainly with the identification of the reaction products and the investigation of the dependence of their cross-sections on the kinetic energies of the colliding species[21-25]. The ion–molecule reactions occurring on photoionisation of hydrogen molecules and helium, neon, and argon atoms and leading to the formation of the ions HeH^+, NeH^+, and ArH^+ have been investigated[26]. It has been shown that the formation of the HeH^+ and NeH^+ ions is associated with the involvement in the ion–molecule reactions of thermal molecular hydrogen ions in excited vibrational states:

$$H_2^+ (^2\Sigma_g, v' \geqslant 3) + He \rightarrow HeH^+ + H , \quad (7)$$

$$H_2^+ (^2\Sigma_g, v' \geqslant 2) + Ne \rightarrow NeH^+ + H . \quad (8)$$

Reactions (7) and (8) are observed for photon energies in excess of 16.20 and 15.97 eV, which corresponds to the formation of secondary HeH^+ and NeH^+ ions from vibrationally excited H_2^+ ions with quantum numbers $v \geqslant 3$ and $v \geqslant 2$ respectively. It has also been shown[26] that the cross-sections of ion–molecule reactions (7) and (8) increase with the vibrational excitation energy of the primary ions.

The formation of HeH^+ and NeH^+ ions involving hydrogen ions in the ground vibrational state is also observed, but in this case the ion–molecule reactions occur at the threshold of the kinetic energy of the initial H_2^+ ions[27].

On the basis of the foregoing data, one may conclude that the ion–molecule reactions leading to the formation of HeH^+ and NeH^+ ions proceed via an intermediate "complex", which ensures a redistribution of the internal and translational energy of the colliding species. It must be noted that the data obtained[26,27] on the role of excited vibrational states of molecules in ion–molecule reactions in hydrogen and noble gases are consistent with the results of the above electron impact studies.

On the basis of the photon energy thresholds for reactions (7) and (8), which are 16.20 and 15.97 eV, it is possible to determine the proton affinities of helium and neon. For helium, this quantity is 1.835 eV, while the proton affinity of neon determined from the energy threshold for reaction (8) is 2.08 eV. This value is consistent with the proton affinity of 2.15 ± 0.3 eV obtained by the electron impact method[21].

Ion–molecule reactions leading to the appearance of ArH^+ ions on photon ionisation of hydrogen and argon are exothermic, since they involve the primary H_2^+ and Ar^+ ions in both ground and excited states:

$$H_2^+ (^2\Sigma_g, v' \geqslant 0) + Ar \rightarrow ArH^+ + H , \quad (9)$$

$$Ar^+ (^2P_{3/2} \text{ or } ^2P_{1/2}) + H_2 \rightarrow ArH^+ + H . \quad (10)$$

With increase of the photon energy from the hydrogen ionisation potential (15.425 eV) upwards, the cross-section of reaction (9) hardly changes, i.e. it is independent of the energy of the vibrational excitation of the initial molecular hydrogen ions. The cross-section of reaction (10), which involves argon ions in the excited state $^2P_{1/2}$, exceeds the cross-section of the same reaction for argon ions in the ground state $^2P_{3/2}$. These results are consistent with the theoretical estimates of the rate constants for the ion–molecule reaction (10).[28]

It has also been shown[26] that the formation of ArH^+ ions begins below the ionisation potentials of the hydrogen molecule and the argon atom for photon energies exceeding the predissociation threshold of the hydrogen molecule in the $D^1\Pi_u$ state (14.66 eV) and therefore may be attributed to the reaction of metastable hydrogen atoms with argon atoms:

$$H(2S) + Ar \rightarrow ArH^+ + e . \quad (11)$$

Argon atoms in the excited electronic state $4d[\frac{1}{2}]_1^0$ (14.71 eV) can also contribute to the formation of ArH^+ and Ar_2^+ ions in collisions with hydrogen molecules and other argon atoms:

$$Ar[4d[1/2]_1^0] + H_2 \rightarrow ArH^+ + (H + e) , \quad (12)$$

$$Ar[4d[1/2]_1^0] + Ar \rightarrow Ar_2^+ + e . \quad (13)$$

The lower limit of the proton affinity of argon determined on the hypothesis that reaction (11) involves thermal hydrogen atoms in the 2S state is 3.397 eV.

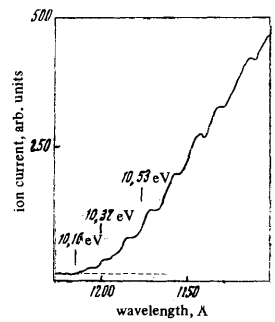

Figure 3. Photoionisation curve for ammonia.

3. Ammonia and Water

The photoionisation of ammonia molecules is characterised by a structure of the vibrational and autoionisation levels on the appearance curve for molecular ions at the first ionisation potential, which is 10.16 eV and corresponds to the removal of an electron from the ^2P_z orbital of the lone electron pair of nitrogen[29-31]. Fig. 3 shows that the initial section of the ammonia photoionisation curve consists of a series of steps, which is evidence of direct ionisation of the molecules in this range of photon

energies. At photon energies of 10.32 and 10.53 eV, the deformation and stretching vibrations of the radical-cations NH_3^+ are excited[30]. A contribution by autoionisation states appears with increase of photon energy.

The formation of excited electronic states of the ammonia radical-cations is observed at higher photon energies (15.31 eV) and involves the removal of an electron from the σ_{NH} orbital[32].

Ion–molecule reactions in ammonia have been investigated by the electron impact method[10,33,34]. Thus, using the method of the pulse withdrawal of ions, it has been shown[10] that the formation of NH_4^+ ions involves radical-cations at thermal velocities, starting with the ammonia ionisation threshold:

$$NH_3^{+\cdot} + NH_3 \rightarrow NH_4^+ + NH_2^{\cdot}. \qquad (14)$$

It has also been shown by the photoionisation method that the appearance potentials of NH_4^+ and $NH_3^{+\cdot}$ ions agree very closely (to within 0.01 eV)[30,31]. These findings suggest that reaction (14) involves the radical-cations $NH_3^{+\cdot}$ in the ground and excited vibrational states.

With increase of photon energy from the primary ionisation potential of ammonia (10.16 eV) upwards by 1.4 eV, the cross-section of the ion–molecule reaction (14) decreases approximately by 20%. This suggests that the yield of NH_4^+ ions in reaction (14) decreases with increasing vibrational excitation of the primary ammonia radical-cations when the vibrational quantum number increases from zero to nine.

Table 1. Heats of formation of molecules, radicals, and ions employed in the thermochemical calculations.

Species	$\Delta H_f^{298°K}$, eV	References	Species	$\Delta H_f^{298°K}$, eV	References
H	+2.26	37	CH_3OH	−2.08	41
NH_2	+1.73±0.08	38	C_2H_5OH	−2.44	41
NH_3	+0.48	39	CH_2O	−1.21	39
NH_4^+	+6.42	36	$CH_3CH{=}O$	−1.72	41
$OH^{\cdot}$	+0.40±0.04	38	$(CH_3)_2CO$	−2.24	39
H_2O	−2.51	39	$CH_3C{=}O^+$	+6.80±0.1	2
H_3O^+	+6.20±0.05	36	CH_3COCH_2	−0.52	38
CH_3O	+0.08±0.09	38	$(CH_3)_2CHOH$	−2.84	41
CH_3OH	−0.35±0.13	38	$(CH_3)_3COH$	−3.24	41
C_2H_5O	−0.30±0.09	38	C_6H_6	+3.12	38
CH_3CHOH^+	−0.80±0.13	38	$C_6H_5CH_2$	+1.92	38
			$C_6H_5^+$	+0.86	39
$CH_2{=}OH^+$	+7.25±0.05	40	$C_6H_5CH_3$	+0.52	39
$CH_3CH{=}OH^+$	+6.10±0.05	40	1,3-$C_6H_4(CH_3)_2$	+0.18	39
$(CH_3)_2COH^+$	+5.10±0.05	40	cyclohexa-1,3-diene	+1.11	39
$CH_3OH_2^+$	+6.00±0.13	11	CH_3	+1.47	38
$C_2H_5OH_2^+$	+5.05±0.4	11			

It has also been shown[31] that the change in the kinetic energy of the primary radical-cations $NH_3^{+\cdot}$, achieved by altering the gradient of the electric field withdrawing ions from the ionisation chamber of the mass-spectrometer, does not affect significantly the variation of the cross-section of reaction (14) with the internal energy of the primary radical-cations. This enabled the authors[31] to conclude that reaction (14) involves the formation of an intermediate "complex" in accordance with the statistical theory of ion–molecule reactions[35]. According to this theory, at the ammonia ionisation threshold reaction (14) proceeds via only one pathway with formation of NH_4^+ ions. With increase of the internal energy of the primary radical-cations $NH_3^{+\cdot}$, the probability of the reverse reaction increases, which leads ultimately to a decrease of the yield of NH_4^+ cations as the photon energy rises.

In contrast to reaction (14), the cross-section for the formation of NH_4^+ ions in the reaction between ammonia radical-cations and water molecules, which involves the transfer of a hydrogen atom, is independent of photon energy in the range from the ionisation potential upwards:

$$NH_3^{+\cdot} + H_2O \rightarrow NH_4^+ + HO^{\cdot}. \qquad (15.1)$$

Another pathway in this reaction involves the formation of H_3O^+ cations by transfer of a proton from the ammonia radical-cation to a water molecule:

$$NH_3^{+\cdot} + H_2O \rightarrow NH_2^{\cdot} + H_3O^+. \qquad (15.2)$$

Thermochemical calculations[36] based on the heats of formation of the cations NH_4^+ and H_3O^+ (Table 1) show that the heats of the exothermic ion-molecule reactions (14), (15.1), and (15.2) are 2.0, 1.3, and 0.2 eV respectively. The proton affinities of ammonia (9.0 eV) and water (7.16 eV) were also determined from the heats of formation of the cations NH_4^+ and H_3O^+.

III. ION–MOLECULE REACTIONS IN SATURATED AND UNSATURATED HYDROCARBONS

1. Olefins

The photoionisation of olefins in the region of the first ionisation potential involves the formation of radical-cations in the ground and excited states as the result of the removal of an electron from an upper π-type molecular orbital, which has a maximum electron density at the C–C bond. The interaction of π electrons with the electrons of the σ orbitals is fairly strong[42].

In the photoionisation of ethylene, deformation and stretching vibrations of the C–C bond at frequencies of 440 and 1400 cm^{-1} respectively are excited in the radical-cations at the ionisation threshold[43]. With increase of photon energy by 1–2 eV, the C–H bond vibrations and combination vibrations at a higher frequency are excited.

The radical-cations thus obtained exhibit a high reactivity in ion–molecule reactions in the photolysis and radiolysis of olefins and unsaturated hydrocarbons.

In the study of ion–molecule reactions in olefins, the mass-spectrometric photoionisation method was first employed by Koyano and coworkers[44,45]. It enabled them to determine various pathways in the formation of secondary products comprising ions of different structures, radicals, and molecules in the reaction between the radical-cations and molecules of the given olefin.

Ethylene[46]:

$$C_2H_4^{+\cdot} + C_2H_4 \rightarrow C_3H_5^+ + CH_3^{\cdot}, \qquad (16.1)$$

$$\rightarrow C_4H_7^+ + H^{\cdot}. \qquad (16.2)$$

Propene[44]:

$$C_3H_6^{+\cdot} + C_3H_6 \rightarrow C_3H_5^+ + C_3H_7^{\cdot} + H_2, \qquad (17.1)$$

$$\rightarrow C_3H_7^+ + C_3H_5^{\cdot}, \qquad (17.2)$$

$$\rightarrow C_4H_7^+ + C_2H_5^{\cdot}, \qquad (17.3)$$

$$\rightarrow C_4H_8^{+\cdot} + C_2H_4, \qquad (17.4)$$

$$\rightarrow C_5H_9^+ + CH_3^{\cdot}. \qquad (17.5)$$

But-1-ene[45]:

$$C_4H_8^{+\cdot} + C_4H_8 \rightarrow C_4H_7^+ + C_4H_9^\cdot , \quad (18.1)$$
$$\rightarrow C_4H_9^+ + C_4H_7^\cdot , \quad (18.2)$$
$$\rightarrow C_5H_9^+ + C_3H_7^\cdot , \quad (18.3)$$
$$\rightarrow C_5H_{10}^{+\cdot} + C_3H_6 , \quad (18.4)$$
$$\rightarrow C_5H_{11}^+ + C_3H_5^\cdot , \quad (18.5)$$
$$\rightarrow C_6H_{11}^+ + C_2H_5^\cdot , \quad (18.6)$$
$$\rightarrow C_6H_{12}^{+\cdot} + C_2H_4 . \quad (18.7)$$

But-2-ene[45]:

$$C_4H_8^+ + C_4H_8 \rightarrow C_4H_7^+ + C_4H_9^\cdot , \quad (19.1)$$
$$\rightarrow C_4H_9^+ + C_4H_7^\cdot , \quad (19.2)$$
$$\rightarrow C_5H_9^+ + C_3H_7^\cdot . \quad (19.3)$$

Isobutene[45]:

$$C_4H_8^{+\cdot} + C_4H_8 \rightarrow C_4H_7^+ + C_4H_9^\cdot , \quad (20.1)$$
$$\rightarrow C_4H_9^+ + C_4H_7^\cdot , \quad (20.2)$$
$$\rightarrow C_5H_9^+ + C_3H_7^\cdot . \quad (20.3)$$

Buta-1,3-diene[44]:

$$C_4H_6^{+\cdot} + C_4H_6 \rightarrow C_3H_3^+ + C_5H_9^\cdot , \quad (21.1)$$
$$\rightarrow C_4H_5^+ + C_4H_7^\cdot , \quad (21.2)$$
$$\rightarrow C_4H_7^+ + C_4H_5^\cdot , \quad (21.3)$$
$$\rightarrow C_6H_6^{+\cdot} + C_3H_6 , \quad (21.4)$$
$$\rightarrow C_5H_7^+ + C_3H_5^\cdot , \quad (21.5)$$
$$\rightarrow C_6H_7^+ + C_2H_5^\cdot , \quad (21.6)$$
$$\rightarrow C_6H_8^{+\cdot} + C_2H_4 , \quad (21.7)$$
$$\rightarrow C_7H_9^+ + CH_3^\cdot . \quad (21.8)$$

The ion–molecule reactions occurring in the photoionisation of olefins involving radical-cations can be divided into three main types.

1. Reactions (18.1), (19.1), (20.1), and (21.1), in which a hydrogen atom is transferred from the radical-cation to the olefin molecule (but-1-ene, but-2-ene, isobutene, and buta-1,3-diene) and which lead to the formation of the corresponding cations and alkyl radicals.

2. Reactions (17.2), (18.2), (19.2), (20.2), and (21.3), which lead to the formation of cations with a mass exceeding the molecular mass by unity and of radicals. It has been shown[47] that reactions of this type in propene and buta-1,3-diene involve the transfer of a hydrogen atom from the molecule to the radical-cation of the olefin.

3. Reactions involving a complex rearrangement of the atoms in the radical-cation and the molecule during collision. This applies in the first place to the formation of secondary ions and neutral species via the dissociation of C–H and C–C bonds in the initial species. Analysis of the velocity distribution of the ion–molecule reaction products in ethylene showed that reactions of this type proceed via a long-lived intermediate "complex", which ensures a redistribution of the energies of the colliding species among different degrees of freedom[45]. However, there are also exceptions for reactions of this type. For instance, the ion–molecule reaction in buta-1,3-diene leading to the formation of $C_3H_3^+$ ions and C_5H_9 radicals involves a direct mechanism.

2. Saturated and Unsaturated Hydrocarbons

Ion–molecule reactions play a significant role in the formation of secondary products in the radiolysis and photolysis of saturated and unsaturated hydrocarbons in the gas phase. The application of the mass-spectrometric photoionisation method permitted the determination of the principal pathways in these ion–molecule reactions and yielded information about the nature of their intermediate states.

Ion–molecule reactions of the first type include processes involving the transfer of H_2^- from the molecule to the radical-cation:

$$C_nH_m^{+\cdot} + AH_2 \rightarrow C_nH_{m+2} + A^{+\cdot} , \quad (22)$$

where AH_2 is a saturated hydrocarbon molecule and $C_nH_m^+$ the radical-cation of an unsaturated hydrocarbon or cyclopropane[48,49]. An example of this type of ion–molecule reactions occurring in the radiolysis of saturated hydrocarbons is the reaction between the propene radical-cations, formed in the decomposition of cyclopentane radical-cations, and cyclopentane molecules[50]:

$$C_3D_6^{+\cdot} + \text{cyclo-}C_5D_{10} \rightarrow C_3D_8 + C_5D_8^{+\cdot} . \quad (22.1)$$

The most systematic data on the mechanism of the ion–molecule reactions occurring in the photolysis of propene and unsaturated hydrocarbons and involving an H_2^- transfer have been obtained by Gorden and Ausloos[51]:

$$C_3D_6^{+\cdot} + AH_2 \rightarrow CD_3CDHCD_2H + A^{+\cdot} , \quad (22.2)$$

where AH_2 is a saturated hydrocarbon molecule (cycloalkanes, straight-chain and branched-chain alkanes). The contribution of other ion–molecule reactions to the formation of secondary products was excluded, since the experiments were performed at a photon energy of 10.0 eV, which is less than the ionisation potentials of the saturated hydrocarbons AH_2.

It is seen that the ion–molecule reaction in the photoionisation of propene and isobutane proceeds via an intermediate state the structure of which ensures the transfer of the HD^- species from the isobutane molecule to the propene radical-cation:

$$C_3D_6^{+\cdot} + (CH_3)_3CD \rightarrow C_3D_7H + C_4H_8^{+\cdot} . \quad (22.3)$$

It has been shown[51] that such an intermediate state ensures the transfer of a hydrogen atom from the CH_3 group of isobutane to the central atom of the $C_3D_6^{+\cdot}$ radical-cation and the formation of the propane molecule CD_3CDHCD_3. Such stereospecificity of the intermediate state in reactions of this type occurs also in the interaction between the propene radical-cation and the n-butane molecule:

$$C_3D_6^{+\cdot} + CD_3CH_2CH_2CD_3 \rightarrow C_3D_7H + CD_2CHCH_2CD_3^{+\cdot} . \quad (22.4)$$

The second important type of ion–molecule reactions in the photoionisation of the molecules in mixtures of saturated and unsaturated hydrocarbons includes H_2 transfer processes[50]:

$$C_nH_m + AH_2^{+\cdot} \rightarrow C_nH_{m+2} + A^{+\cdot} , \quad (23)$$

where C_nH_m is a cyclopropane or an unsaturated hydrocarbon molecule and $AH_2^{+\cdot}$ is the radical-cation of a saturated hydrocarbon. This type of reaction between the cyclohexane radical-cation and the cyclopropane molecule,

$$\text{cyclo-}C_6H_{12}^{+\cdot} + \text{cyclo-}C_3D_6 \rightarrow C_6H_{10}^{+\cdot} + C_3D_6H_2 , \quad (23.1)$$

involves the transfer of H_2 from the radical-cation and its addition to two carbon atoms with simultaneous ring opening and the formation of the propane molecule $CD_2HCD_2.CD_2H$.

It should be noted that in ion–molecule reactions of type (23), there is a competing process involving the

transfer of a hydrogen atom from the radical-cation to the molecule:

$$C_nH_m + AH_2^{+\cdot} \rightarrow C_nH_{m+1}^{\cdot} + AH^+. \quad (24)$$

Ion–molecule reactions at a high pressure (p = 20 torr) in a mixture of cyclobutane with saturated hydrocarbons, aliphatic amines, and other compounds have been investigated by the photoionisation method[52].

In a mixture of cyclobutane with alkanes and cycloalkanes, ion–molecule reactions proceeding via two pathways were observed: via the transfer of H^- and H_2^- from the AH_2 molecule (alkane or cycloalkane) to the radical-cation $C_4H_8^{+\cdot}$ formed in the photoionisation of cyclobutane ($h\nu \simeq 10.3$ eV):

$$C_4H_8^{+\cdot} + AH_2 \rightarrow C_4H_9^{\cdot} + AH^+, \quad (25.1)$$

$$C_4H_8^{+\cdot} + AH_2 \rightarrow C_4H_{10} + A^{+\cdot}. \quad (25.2)$$

Ion–molecule reactions involving charge transfer in mixtures of cyclobutane with cyclohexane, trimethylamine, and nitric oxide were also observed in the same study.

IV. PHOTOIONISATION AND ION–MOLECULE REACTIONS IN KETONES AND ALCOHOLS

1. Alcohols

Systematic studies on the primary photoionisation and decomposition processes of aliphatic alcohols were first performed by Potapov and Sorokin[40] and Refaye and Chupka[53]. The application of the accurate photoionisation method made it possible to resolve the structure of the electronic and vibrational levels of the radical-cations on the photoionisation curves for alcohols recorded automatically on an MKh-1311 mass-spectrometer[1] and to determine the formation energies of fragment ions of different structures.

It was shown that ethanol radical-cations are formed mainly in excited electronic states at photon energies of 10.49 and 11.6 eV, which correspond to the removal of an electron from the $n(2P_y)$ orbital of the lone pair of oxygen and from the highest occupied σ orbital of the ground state respectively[40].

Data on the nature of the vibrational states of methanol and ethanol radical-cations excited in photoionisation have been obtained[40] by automatic differentiation of the initial sections of the photoionisation curves. The vibrational spectra of methanol (CD_3OH, CH_3OH, and CH_3OD) radical-cations shown in Fig. 4 are characterised by the presence of two principal bands. The first band (0–0 transition) corresponds to the first adiabatic ionisation potential of methanol, involving the removal of an electron from the lone pair of oxygen. The second band (900 cm^{-1}) may be assigned to the excitation of vibrations associated with the C–O bond. The relative intensity of these vibrations does not change when the hydrogen atom is substituted by a deuterium atom in the hydroxy-group but increases when the three hydrogen atoms in the methyl group are replaced by deuterium atoms. The probability of the formation of vibrationally excited radical-cations of ethanol is higher than the probability of their formation in the ground state. These findings indicate an increase of the C–O equilibrium bond length in the radical-cation on passing from CH_3OH to CD_3OH and C_2H_5OH.

Data on the mechanism of the decomposition of methanol and ethanol radical-cations on photoionisation were obtained[40] by analysing the simple mass spectra and appearance potentials of the fragment ions of the deuterated compounds CD_3OH and CH_3CD_2OH:

$$CD_3OH + h\nu \rightarrow CD_3OH^{+\cdot} + e, \quad (26.1)$$

$$CD_2OH^+ + D + e, \quad (26.2)$$

$$CH_3CD_2OH + h\nu \rightarrow CH_3CD_2OH^{+\cdot} + e, \quad (27.1)$$

$$CH_3CDOH^+ + D + e, \quad (27.2)$$

$$CD_2OH^+ + CH_3 + e. \quad (27.3)$$

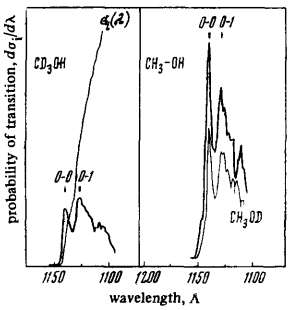

Figure 4. Vibrational spectra of radical cations.

Table 2. Appearance potentials of methanol and ethanol ions.

Compound	m/e	Type of ion	Appearance potential, eV
CD_3OH	35	$CD_3OH^{+\cdot}$	10.85±0.01
	34	$(CD_3O)^+$	12.0±0.05
	33	$CD_2{=}\overset{+}{O}H$	11.6±0.05
CH_3CD_2OH	48	$CH_3CD_2OH^{+\cdot}$	10.49±0.01 11.6±0.1
	46	$CH_3CD{=}\overset{+}{O}H$	10.8±0.05 11.7±0.1
	33	$CD_2{=}\overset{+}{O}H$	11.2±0.05
t-C_4H_9OH	59	$(CH_3)_2C{=}\overset{+}{O}H$	9.87±0.05 11.0±0.1 12.2±0.2

Table 2 shows that the decomposition processes which are energetically the most favourable are the decomposition reactions involving the dissociation of C–D and C–C bonds in the vibrationally excited radical-cations [reactions (26.2) and (27.2)] obtained by the removal of an electron from the lone pair of oxygen. These reactions involve a change in the initial electronic-nuclear configuration of the radical-cations with formation of the cations $CD_2{=}\overset{+}{O}H$ and $CH_3CD{=}\overset{+}{O}H$. The formation of $(CD_3O)^+$ ions from methanol is observed at a photon energy of 12.0 eV, which exceeds by 0.4 eV the appearance potential of the $CD_2{=}\overset{+}{O}H$ ions derived from CD_3OH [reaction (26.2)], but their yield is low. The $(CD_3O)^+$ ions formed via a rearrangement of the hydrogen and deuterium atoms have a structure of the type $CH_2{=}\overset{+}{O}H$, since the formation of CD_3O^+ ions by a direct removal of an electron from the σ orbital should occur at higher energies.

It is noteworthy that, according to the data of Brehm et al. [55], the dissociative photoionisation of methanol in the range of energies between the first and second ionisation potentials can also proceed via autoionisation states. However, in the case of ethanol the contribution by autoionisation states to the formation of fragment ions is already insignificant. The formation of $(CH_3CDOH)^+$ ions from CH_3CD_2OH at a photon energy of 11.7 eV, i.e. higher by 0.1 eV than the second ionisation potential, is associated with the decomposition of electronically excited radical-cations.

A characteristic feature of the photoionisation of t-butyl alochol [40] is the absence from the mass spectrum of an appreciable yield of molecular ions. The main dissociation process of t-butyl alcohol is the formation of $(CH_3)_2C{=}\overset{+}{O}H$ cations and methyl radicals in the range of energies from 9.87 eV upwards:

$$(CH_3)_3COH + h\nu \rightarrow (CH_3)_2C{=}\overset{+}{O}H + CH_3 + e \quad . \qquad (28)$$

The yield of $(CH_3)_2C{=}\overset{+}{O}H$ cations increases appreciably at energies of 11.0 and 12.2 eV, corresponding to the second and third ionisation potentials of the t-butyl alcohol molecule.

Table 3. Ion–molecule reactions in methanol and ethanol [46].

Reactions		$-Q^{298°K}$*, eV	Reaction cross-section**
$CH_3OD^{+\cdot} + CH_3OD \rightarrow CH_3\overset{+}{O}D_2 + CH_3O$	(29.1)	0.6±0.1	1.0
$\rightarrow CH_3\overset{+}{O}DH + CH_2OD$	(29.2)	1.0±0.1	0.6
$CH_2\overset{+}{O}D + CH_3OD \rightarrow CH_3\overset{+}{O}D_2 + CH_2O$	(29.3)	0.4±0.1	2.7
$CH_3CD_2OH^{+\cdot} + CH_3CD_2OH \rightarrow CH_3CD_2\overset{+}{O}H_2 + CH_3CD_2O$	(30.1)	0.9±0.4	1.0
$CH_3CD_2OH^{+\cdot} + CH_3CD_2OH \rightarrow CH_3CD_2\overset{+}{O}HD + CH_3CDOH$	(30.2)	1.2±0.4	0.3
$\rightarrow CH_3CD_2\overset{+}{O}H_2 + CH_2CD_2OH$	(30.3)	1.2±0.4	0.06
$CD_2\overset{+}{O}H + CH_3CD_2OH \rightarrow CH_3CD_2\overset{+}{O}H_2 + CD_2O$	(30.5)	0.8±0.4	1.5
$CH_3CD\overset{+}{O}H + CH_3CD_2OH \rightarrow CH_3CD_2\overset{+}{O}H_2 + CH_3CDO$	(30.6)	0.2±0.4	

*Q is the heat of the ion–molecule reaction.
**The relative cross-sections for the reaction paths indicated in the Table correspond to a single dissociated bond.

The ion–molecule reactions occurring in the photon ionisation of methanol and ethanol [54] are exothermic, since the appearance potentials of the secondary cations agree to within 0.02 eV with the first ionisation potentials of methanol (10.85 eV) and ethanol (10.49 eV). This finding is consistent with data for ion–molecule reactions in alcohols obtained by the electron impact method using pulse withdrawal of ions [11].

Analysis of the changes in the mass spectra of methanol (CD_3OH, CH_3OD) and ethanol (CH_3CD_2OH, CD_3CH_2OH) as a function of the concentration of the alcohol in the ionisation chamber and of photon energy, carried out by Potapov and Sorokin [54], made it possible to determine the relative cross-sections for different pathways of ion–molecule reactions in both methanol and ethanol.

Table 3 shows that a general characteristic of ion–molecule reactions in alcohols involving primary radical-cations is that reactions (29.1) and (30.1), which yield secondary oxonium cations and the alkoxy-radicals CH_3O and CH_3CD_2O respectively, are more probable than reactions (29.2) and (30.2) involving the formation of secondary cations and methanol and ethanol radicals, despite the fact that the latter processes are energetically more favourable. In ethanol oxonium cations and the radicals CH_2CD_2OH are also formed but with a lower probability than that of the processes described above.

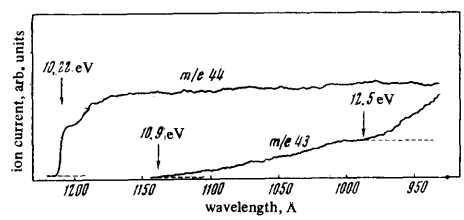

Figure 5. Appearance curves for molecular and fragment ions of acetaldehyde.

The different probabilities of ion–molecule reactions in alcohols by various pathways are determined by the interaction of the positive ion with the induced molecular dipole, which is a specific feature of polar molecules. In this case such an interaction between the radical-cation and the molecule leads to preliminary orientation of the molecule relative to the ion, which ensures the maximum probability of the ion–molecule reaction involving the transfer of a hydrogen atom (proton) from the O–H group. The probability of the reaction via this pathway relative to the reaction yielding secondary cations and radicals by the dissociation of the C_α–H bond is higher in ethanol than in methanol, probably owing to the greater polarisability of ethanol.

As already mentioned above, the electronic states of the methanol and ethanol radical-cations formed by the removal of an electron from the lone pairs of oxygen are characterised by the presence of a free valence localised at the oxygen atomic orbital. This explains the high reactivity of the alcohol radical-cations in their decomposition into cations of the type $CH_2{=}\overset{+}{O}H$ (methanol) and $CH_3CH{=}\overset{+}{O}H$ (ethanol). This feature should of course be observed also in ion–molecule reactions involving methanol and ethanol radical-cations. For this reason, one may postulate that the formation of heavier ions and radicals proceeds via the dissociation of the O–H (C–H) bond in the molecule and the addition of a hydrogen atom to the free valence of the radical-cation. This naturally does not rule out the possibility that ion–molecule reactions involving radical-cations can proceed via a proton transfer, for example from the OH group of the radical-cation to the molecule.

It has been shown [30,54] that near the first ionisation potentials the cross-sections of ion–molecule reactions in methanol and ethanol involving radical-cations are independent of the energy of the ionising photons and hence of the vibrational excitation of the radical-cations on photoionisation (Fig. 6). For reactions (29.2) and (30.2), which

lead to the formation of oxonium ions and methanol and ethanol radicals, the variation of the cross-section with photon energy persists also at photon energies exceeding the second ionisation potential of ethanol. This type of relation between the ionisation cross-sections for ion–molecule reactions and the internal energy of radical-cations is characteristic of processes involving the transfer of a hydrogen atom.

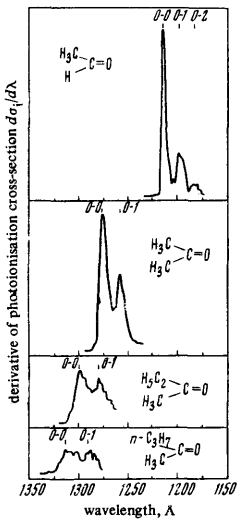

Figure 6. Vibrational spectra of the radical-cations of aliphatic ketones.

The cross-sections of ion–molecule reactions leading to the formation of oxonium ions $CH_3\overset{+}{O}D_2$ from CH_3OD and $CH_3CD_2\overset{+}{O}H_2$ from CH_3CD_2OH begin to increase at photon energies coresponding to the appearance potentials of the cations $CH_2{=}\overset{+}{O}D$ (CH_3OD) and $CH_3CD{=}\overset{+}{O}H$ (CH_3CD_2OH). This finding is evidence of the involvement of the cations $CH_2{=}\overset{+}{O}H$, $CH_3CD{=}\overset{+}{O}H$ and $CD_2{=}\overset{+}{O}H$ in the ion–molecule reactions (29.3), (30.4), and (30.5). This conclusion is consistent with the hypothesis of the involvement in ion–molecule reactions of fragment ions formed by electron impact[56]. Table 3 shows that these reactions are exothermic and proceed via the transfer of a proton from the hydroxy-group of the cation to the molecule with formation of the corresponding secondary oxonium ions and formaldehyde and acetaldehyde molecules.

2. Ketones

A characteristic feature of the electronic structure of aliphatic ketones is that the upper level of the ground state is occupied by the lone electron pair of oxygen[57]. This feature is clearly reflected in the presence of sharply rising sections in the photoionisation curves for acetaldehyde and acetone (see, for example, Fig. 5) near the first ionisation potentials, corresponding to the formation of radical-cations in the ground vibrational state by the removal of an electron from the $n(2P_y)$ orbital of the carbonyl oxygen[2]. The electronic states of the radical-cations formed in this way are characterised by the presence of a free valence localised at the atomic orbital of the heteroatom.

The vibrational spectra of the radical-cations of acetaldehyde, acetone, ethyl methyl ketone, and methyl n-propyl ketone, obtained by the automatic differentiation of the initial sections of the photoionisation curves and presented in Fig. 6, indicate the position of the 0–0 transition corresponding to the adiabatic ionisation potential and the 0–1 transition associated with the excitation of the vibrations of the C–O bond in the radical-cation[40]. The energies of these vibrations are in the range 0.14–0.15 eV for all the ketones mentioned above. This assignment of the vibrational bands of the radical-cations is consistent with data[58] showing that the vibrational energy of the C=O group in ketones, in excited electronic states, is of the order of 0.16 eV. The relative probability of the formation of the ketone radical-cations in the vibrational ground state, formed by the removal of an electron from the lone pair of oxygen, is a maximum, It decreases on passing from acetaldehyde to methyl n-propyl ketone, which is evidence that, with increase in the length of the aliphatic chain, the change in the equilibrium internuclear distance in the C=O bond of the radical-cations increases compared with the equilibrium internuclear distance in molecules in the ground state. It is of course reflected in a decrease of the relative intensity of the electronic 0–0 transition compared with the intensity of the 0–1 band corresponding to the C=O bond vibration. The mechanism of the interaction of the electrons of the radical-cation, leading to a change in bond length and order, depends on the change in the degree of overlap of the wave function of the unpaired electron of the lone pair of oxygen with the wave functions of the σ and π orbitals on passing from acetaldehyde to methyl n-propyl ketone.

The decrease in the adiabatic ionisation potentials of the ketones of the above series is correlated with the decrease of the C=O bond order of the molecule in the ground state and it has been shown[59] to be related to the increased polarity of this bond (increased negative charge at the oxygen atom).

At higher vibrational excitation energies, i.e. at ionising photon energies of 10.89 eV (acetaldehyde) and 10.42 eV (acetone), the interaction of the unpaired oxygen electron with the electrons of the σ orbitals leads to a change of the electronic-nuclear configuration of the radical-cation as a whole and its decomposition into the ion $CH_3-C{\equiv}O^+$ and the radical R:

$$\begin{matrix} R \\ H_3C \end{matrix}\!\!>\!C{=}O + h\nu \rightarrow \begin{matrix} R \\ H_3C \end{matrix}\!\!>\!C{=}O^{+\cdot} + e\ , \qquad (31.1)$$

$$\rightarrow CH_3{-}C{\equiv}O^{+} + R + e\ , \qquad (31.2)$$

where R = H or CH_3.

In the region of photon energies of 11.7 eV, the appearance curve for fragment ions of acetone shows an appreciable increase of the yield of the ions. The increased yield for this energy may be attributed to the decomposition of electronically excited acetone radical-cations:

$$(CH_3)_2CO + h\nu \rightarrow CH_3{-}\overset{+}{C}{=}O + CH_3 + e\ . \qquad (32)$$

The cations formed in this way have a structure different from that of $CH_3-C{\equiv}\overset{+}{O}$ formed in the decomposition of vibrationally excited radical-cations by reaction (31.2). For acetaldehyde, the formation of fragment ions with a mass of 43 by this pathway takes place at a higher energy (12.5 eV), corresponding to the second ionisation potential.

It has been shown[30] that at higher vapour pressures of acetaldehyde and acetone the mass spectra of these compounds reveal secondary cations, the origin of which may be accounted for as follows. In the collisions between radical-cations and molecules, the unpaired electron of the heteroatom enters into an exchange interaction with the electrons of the C–H bond of the molecule, which may become very intense (in the presence of the necessary overlapping of the electron clouds of the colliding species) and may lead to the dissociation of the C–H bond and the formation of a new bond in the ion:

$$CH_3CH=\overset{+\cdot}{O} + CH_3CH=O \rightarrow CH_3CH=\overset{+}{O}-H + CH_3CO\,, \qquad (33)$$

$$(CH_3)_2C=\overset{+\cdot}{O} + (CH_3)_2C=O \rightarrow (CH_3)_2C=\overset{+}{O}-H + CH_3COCH_2\,. \qquad (34)$$

The heats of the exothermic ion–molecule reactions (33) and (34) involving the transfer of a hydrogen atom, determined from the heats of formation of the reactant species, are −0.87 and −0.75 eV. The cross-section of reactions (33) and (34) in the range of photon energies between the first ionisation potential of acetaldehyde (10.22 eV) and acetone (9.71 eV) and above are independent of the photon energies. The increase of the yield of secondary cations, observed, for example, for acetone at an energy of 11.7 eV, is probably associated with the participation of cations formed in the decomposition of the molecule via mechanism (32):

$$CH_3-\overset{+}{C}=O + (CH_3)_2CO \rightarrow [(CH_3)_2COH]^+ + CH_3CO\,. \qquad (35)$$

Reaction (35) involves the dissociation of two bonds and the formation of two new bonds, the bond dissociation and formation processes occurring simultaneously in a single step during the collision period, i.e. via an intermediate "complex". Cations of the type $R-C\equiv\overset{+}{O}$ do not contribute to the formation of secondary cations, since thermochemical calculation shows that ion–molecule reactions with their participation are endothermic.

The knowledge of the heats of formation of the ions $CH_2=\overset{+}{O}H$, $CH_3CH=\overset{+}{O}H$, and $(CH_3)_2C=\overset{+}{O}H$, obtained by the photoionisation method[40], permits the determination of the proton affinities of formaldehyde (7.4 ± 0.05 eV), acetaldehyde (8.05 ± 0.05 eV), and acetone (8.5 ± 0.1 eV).

Studies on the photoionisation processes of acetone at a pressure of 10^{-3}–10^{-2} mmHg[68] led to the observation of ion–molecule reactions leading to the formation of a high yield of the associated ions M_2^+ and $(M+1).M_n^+$, where $n = 1, 2,$ or 3.

3. Ketones and Alcohols

Ion–molecule reactions in the photoionisation of the molecules in mixtures of ketones and alcohols have been investigated[60]. To identify different pathways of such reactions, deuterated specimens of acetone and ethanol were employed.

Analysis of the mass spectra of the molecules in the binary systems $(CH_3)_2CO-C_2H_5OD$ and $(CD_3)_2CO-C_2H_5OH$ showed that reactions involving acetone and ethanol radical-cations have the following mechanisms:

$$(CH_3)_2CO^{+\cdot} + C_2H_5OD \rightarrow (CH_3)_2C\overset{+}{O}D + C_2H_5O\,, \qquad (36)$$

$$(CD_3)_2CO + C_2H_5OH^{+\cdot} \rightarrow CD_3COCD_2 + C_2H_5OHD^+\,. \qquad (37.1)$$

The formation of the stable ions $(CH_3)_2C\overset{+}{O}D$ and $C_2H_5\overset{+}{O}HD$ involves the transfer of a deuterium atom from the molecules to the radical-cations $(CH_3)_2CO^{+\cdot}$ and $C_2H_5OH^{+\cdot}$ in the range of photon energies between the ionisation potentials of acetone (9.71 eV) and ethanol (10.49 eV) and above. Thermochemical calculation shows that the heats of these exothermic reactions [reactions (1) and (2)] are respectively −0.25 and −1.3 eV.

It has also been shown[60] that at photon energies from the ionisation potential of C_2H_5OD (10.48 eV) upwards, rapid formation of $(CH_3)_2C=\overset{+}{O}D$ ions is observed, which suggests that they are produced in reactions of molecular and fragment ions of C_2H_5OD with the molecules of acetone $(CH_3)_2CO$:

$$(CH_3)_2CO + C_2H_5OD^{+\cdot} \rightarrow (CH_3)_2C=\overset{+}{O}D + C_2H_5O\,, \qquad (37.2)$$

$$(CH_3)_2CO + CH_3CH=\overset{+}{O}D \rightarrow (CH_3)_2C=\overset{+}{O}D + CH_3CHO\,, \qquad (38)$$

$$(CH_3)_2CO + CH_2=\overset{+}{O}D \rightarrow (CH_3)_2C=\overset{+}{O}D + CH_2O\,. \qquad (39)$$

Reactions (37.2), (38), and (39) are exothermic (the heats are −1.0, −0.48, and −1.13 eV) and involve the transfer of a deuteron from ethanol ions to acetone. In this case the deuteron adds to the lone pair of oxygen. The neutral products of this reaction are the ethoxy-radical, acetaldehyde, and formaldehyde respectively. It is noteworthy that the fragment ions of ethanol make the principal contribution to the yield of the proton-transfer reactions between acetone and ethanol.

The reactions between the ions and the molecules of acetophenone and ethanol also proceed via two pathways. The reaction of the acetophenone radical-cations with ethanol molecules is accompanied by the transfer of a deuterium atom from C_2H_5OD and its addition at the oxygen free valence in the acetophenone radical-cation:

$$H_5C_6-\underset{H_3C}{C}=O^{+\cdot} + C_2H_5OD \rightarrow C_6H_5-\underset{H_3C}{C}=\overset{+}{O}D + C_2H_5O\,. \qquad (40)$$

The increase of the yield of the secondary acetophenone ions $C_6H_5\overset{+}{C}ODCH_3$ in the range of photon energies from 10.8 eV upwards is probably associated with reactions involving the transfer of a deuteron from ethanol fragment ions to the acetophenone molecule:

$$H_5C_6\diagdown\underset{H_3C}{}\!\!>C=O + CH_3CH=\overset{+}{O}D \rightarrow H_5C_6\diagdown\underset{H_3C}{}\!\!>C=\overset{+}{O}D + CH_3CHO\,, \qquad (41)$$

$$H_5C_6\diagdown\underset{H_3C}{}\!\!>C=O + CH_2=\overset{+}{O}D \rightarrow H_5C_6\diagdown\underset{H_3C}{}\!\!>C=\overset{+}{O}D + CH_2O\,. \qquad (42)$$

The ion–molecule reactions in ketones and alcohols involve the radical-cations formed by the removal of an electron from the upper orbital of the lone pair of the heteroatom and fragment ions. The reactions of the radical-cations with molecules involve the transfer of a hydrogen atom from the molecule to the radical-cation. The hydrogen atom adds to the heteroatom, which has a free valence, without a significant change in the structure of the radical-cations, i.e. without a complete redistribution of the energies of the colliding species among the degrees of freedom during the period of their interaction. This conclusion is confirmed by the independence of the cross-sections for these ion–molecule reactions of the excitation energy of the initial radical-cations. The reactions of the alcohol fragment ions with the molecules of alcohols and ketones take place via the transfer of a proton from the OH group of the fragment ion to the molecule. Here it is noteworthy that processes of this type make the principal contribution to the formation of the secondary ion–molecule reaction products in alcohols and ketones.

V. ION–MOLECULE REACTIONS IN AROMATIC HYDROCARBONS

Studies on ion–molecule reactions in aromatic hydrocarbons by the electron impact method have shown[61–63] that the formation of secondary products involves only fragment ions produced by the ionisation of the molecules (benzene, toluene). In these studies the failure to observe ion–molecule reactions between radical-cations and molecules which are not prohibited on energy grounds shows the passivity of the electronic states of the radical-cations of aromatic hydrocarbons produced by the removal of an electron from the π orbital of the ground state.

The problem of the mechanism of the ion–molecule reactions occurring in the photoionisation of "aromatic hydrocarbon–alcohol" mixtures was examined by Potapov and Sorokin[64]. To identify the reactions between ions and molecules of the "benzene–ethanol" system, two mixtures, $C_6D_6-C_2H_5OH$ and $C_6H_6-C_2H_5OD$, were chosen. By analysing the variation of the mass spectrum of the molecules of the mixtures with photon energy and concentration of the components, it was shown that the ion–molecule reactions in benzene and ethanol proceed via two paths (Fig. 7*a*):

$$C_6D_6 + C_2H_5OH^{+\cdot} \rightarrow C_6D_5 + C_2H_5OHD^+ , \quad (43)$$

$$C_6H_6 + CH_2{=}\overset{+}{O}D\,(C_2H_5OD) \rightarrow C_6H_6D^+ + CH_2O . \quad (44)$$

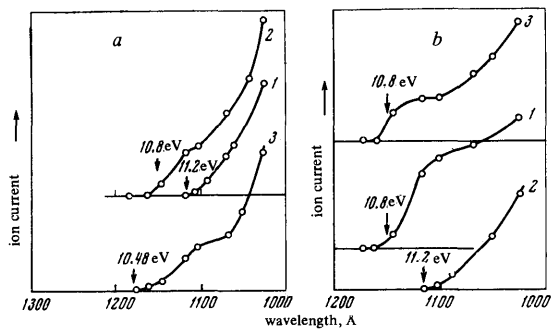

Figure 7. *a*) Appearance curves for the secondary ions of $C_6H_6D^+$ (curve *1*), toluene $C_7H_8D^+$ (curve *2*), and *m*-xylene $C_8H_{10}D^+$ (curve *3*); *b*) appearance curves for the primary ions of deuteroethanol CH_2OD^+ (curve *2*) and CH_3CHOD^+ (curve *1*) and secondary ions of naphthalene $C_{10}H_8D^+$ (curve *3*).

The heat of the exothermic reaction (43), involving the transfer of a deuterium atom from benzene to the radical-cation with formation of phenyl radicals, is 0.73 eV. Reaction (44), in which the benzene cations $C_6H_6D^+$ are formed, involves the transfer of a deuteron from the hydroxy-group of the $CH_2{=}\overset{+}{O}D$ cation. This is indicated by the identity of the appearance potentials of the $C_6H_6D^+$ and $CH_2{=}\overset{+}{O}D$ cations. This conclusion is consistent with data for the formation of $C_6H_7^+$ ions in benzene and ethanol, which was observed by the electron impact method at higher energies[65].

The appearance potentials of the secondary and primary ions show that three ion–molecule reactions take place between toluene and ethanol ($C_6D_5CD_3-C_2H_5OH$ and $C_6H_5CH_3-C_2H_5OD$ mixtures)[64]:

$$C_6D_5CD_3 + C_2H_5OH^{+\cdot} \rightarrow C_6H_5CD_2 + C_2H_5OHD^+ , \quad (45)$$

$$C_6H_5CH_3 + CH_3CHOD^+\,(C_2H_5OD) \rightarrow C_7H_8D^+ + CH_3CHO , \quad (46.1)$$

$$C_6H_5CH_3 + CH_2OD^+\,(C_2H_5OD) \rightarrow C_7H_8D^+ + CH_2O . \quad (46.2)$$

In contrast to the reactions in benzene and ethanol, in the "toluene–ethanol" system the secondary cations $C_7H_8D^+$ are formed by the transfer of a deuteron from the cation CH_3CHOD^+, which is evidence of a similarity of the appearance potentials of the cations $C_7H_8D^+$ and CH_3CHOD^+. A comparative estimate of the heats of ion–molecule reactions in toluene and ethanol showed that the cations $C_7H_8D^+$ can also be formed as a result of the transfer of a deuteron from the radical-cation $C_2H_5OD^{+\cdot}$. However, the yield of this reaction is probably much lower than those of reactions (46) and (47).

Ion–molecule reactions in *m*-xylene and ethanol, involving the transfer of protons from the ethanol radical-cation and fragment ions of the above type, have also been observed[64].

In view of the occurrence of the exothermic reactions (44) and (46), it is possible to determine the lower limits of the proton affinities of benzene and toluene: 7.44 and 8.05 eV. The proton affinity obtained for benzene agrees well with the value 7.46 eV determined[64] by the photoionisation method from the appearance potential of $C_6H_7^+$ ions derived from cyclohexa-1,3-diene.

The ion–molecule reactions occurring in the photoionisation of the molecules of "naphthalene–ethanol" and "anthracene–t-butyl alcohol" mixtures have been investigated[66] and it was shown that the secondary cations of naphthalene $C_{10}H_8D^+$ (see Fig. 7*b*) and anthracene $C_{14}H_{11}^+$ are formed in the reactions by the transfer of deuterons (protons) from the alcohol cations to the molecules of the aromatic hydrocarbons:

$$C_{10}H_8 + CH_3CHOD^+\,(C_2H_5OD) \rightarrow C_{10}H_8D^+ + CH_3CHO , \quad (47.1)$$

$$C_{10}H_8 + CH_2OD^+\,(C_2H_5OD) \rightarrow C_{10}H_8D^+ + CH_2O , \quad (47.2)$$

$$C_{14}H_{10} + (CH_3)_2COH^+\,((CH_3)_3COH) \rightarrow C_{14}H_{11}^+ + (CH_3)_2CO . \quad (48)$$

The lower limits of the proton affinities of naphthalene and anthracene determined from reactions (47.1) and (48) are respectively 8.05 and 8.5 eV.

Ion–molecule reactions involving the radical-cations of aromatic hydrocarbons A and leading to the formation of the cations AH^+ have not been observed[64,66]. Thermochemical calculation shows that in benzene and toluene reactions of this type are endothermic. However, as already mentioned above, despite the absence of an energy prohibition, bimolecular ion–molecule reactions involving benzene and toluene radical-cations also do not occur[61,62].

The low reactivity of the radical-cations of aromatic hydrocarbons may be due to the nature of the electronic states of the radical-cations generated on photoionisation by the removal of an electron from the occupied molecular π orbitals.

Trimolecular ion–molecule reactions involving the molecular ions of benzene and leading to the formation of the ions $C_{12}H_{12}^+$ have been observed[69]. The excess excitation energy of the "complex" is removed in this case by a third body.

VI. PROTON AFFINITY OF MOLECULES

Data on photoionisation and ion–molecule reactions yielded information about the structural characteristics of

the molecules A which determine their capacity to form stable cations AH^+ by combining with a proton. The stability of the cations is determined by the proton affinities of the compounds, which are listed in Table 4.

The formation of the cations AH^+ by aliphatic compounds containing the $\rangle C{=}O$ and O–H groups takes place as the result of the addition of a proton to the lone pair of electrons of the heteroatom. The stability of the alcohol cation increases on passing from methanol to ethanol, i.e. on replacement of a hydrogen atom by a methyl group, which results in an increase of electron density at the oxygen atom. In this case the proton affinity increases from 7.8 eV (methanol) to 8.4 eV (ethanol). The same type of variation in the stability of the cations is observed in the series formaldehyde < acetaldehyde < acetone. The proton affinity of these molecules increases from 7.4 to 8.5 eV for the same reason.

Table 4. Proton affinities of atoms and molecules.

Compound	Proton affinity, eV	Method of determination	References
H	2.70	Photoionisation	3
H_2	3.40	Chemi-ionisation	3
He	1.83	IMR in photoionisation	26
Ne	2.83	IMR in photoionisation	26
Ar	3.40	Chemi-ionisation	26
NH_3	9.0±0.05	Electron impact	36
H_2O	7.16±0.05	Electron impact	36
CH_3OH	7.8±0.13	IMR in electron impact	11
C_2H_5OH	8.4±0.4	IMR in electron impact	11
CH_2O	7.40±0.05	Photoionisation	60
CH_3CHO	8.05±0.05	Photoionisation	60
$(CH_3)_2CO$	8.5±0.05	Photoionisation	60
C_6H_6	7.46±0.03	Photoionisation	64
$C_6H_5CH_3$	8.05	IMR in photoionisation	64
Naphthalene	8.05	IMR in photoionisation	66
Anthracene	8.5	IMR in photoionisation	66

In aromatic hydrocarbons the stability of the cations formed in ion–molecule reactions increases with the number of rings, i.e. with decrease of the localisation energy, which is equal to the difference between the energies of the π-electron systems of the cation AH^+ and the molecule A. This feature is clearly reflected in the ion–molecule reactions involving aromatic hydrocarbons and alcohols and leading to the formation of the cations AH^+ as a result of proton transfer, and allows the conclusion that the addition of a proton to aromatic hydrocarbon molecules takes place by an electrophilic substitution mechanism. This implies that the proton adds to the carbon atom at which the π-electron density is a maximum and is accompanied by the formation of the cations AH^+ with the structure of a σ complex.

The high stability of the AH^+ cations of benzene, naphthalene, and anthracene formed in ion–molecule reactions (the affinity increases from 7.46 to 8.5 eV) is determined by the formation of a new σ_{CH} bond and a marked polarisation interaction, which becomes more intense with increasing number of π electrons in the aromatic hydrocarbons. The substitution of hydrogen atoms in benzene by an electron-donating group such as CH_3 also leads to an increase of the stability of the cations AH^+.

The data obtained on the stabilities of the cations are correlated with the basicity constants of the aromatic hydrocarbons[67].

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Chemically Induced Polarisation of Electrons and Nuclei

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The polarisation, in excess of the equilibrium value, of electrons and nuclei in the species generated in chemical reactions was observed in ESR and NMR spectra quite recently and during the last 2-3 years studies of this kind have developed vigorously. The aim of the present review is to present the principal results of studies on chemically induced polarisation of electrons and nuclei, to formulate the ideas and concepts concerning the nature of the phenomena discussed, and also to attempt an assessment of their importance and prospects.
The bibliography includes 70 references.

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I. INTRODUCTION

The ESR or NMR spectrum of a radical, ion, or molecule constitutes a kind of "portrait" of the species or fragment. The spectra contain information about the chemical structure of the species, its orientation (in a solid), the frequencies of molecular motion, and the energies of electron–electron and electron–nucleus magnetic interactions.

The usual magnetic resonance spectra do not of course provide any information about the elementary steps in the generation of the species, i.e. about the nature of the states preceding the species. The reason for this is that the magnetic resonance spectra usually recorded are the absorption spectra of the species in which the populations of the magnetic Zeeman (electronic or nuclear) levels correspond to thermal equilibrium, i.e. obey the Boltzmann distribution. However, in the steps involving the generation of the species (radicals or molecules) or in the states from which these species are produced (triplet states, radical pairs, etc.), there is a possibility of a non-equilibrium population of the Zeeman levels. Then the species generated will not give rise to the usual magnetic resonance spectra corresponding to equilibrium absorption but to spectra with an anomalously strong absorption or to emission spectra. The first case corresponds to positive polarisation of electrons or nuclei in the species in excess of the equilibrium value and the second to negative polarisation.

The observation of the effects of non-equilibrium polarisation of electrons or nuclei in ESR or NMR spectra is of course only possible immediately after the generation of the species when they "remember" the non-equilibrium polarisation induced in them during the electronic (10^{-7}–10^{-5} s) or nuclear (1–30 s) relaxation time; after this period, the species lose their polarisation in excess of the equilibrium value.

II. CHEMICALLY INDUCED NUCLEAR POLARISATION

Chemically induced nuclear polarisation (CINP)† is shown in the NMR spectra of the products of reactions occurring in the magnetic field of the NMR spectrometer. It is observed as an intense radiofrequency absorption (positive polarisation) or a radiofrequency emission (negative polarisation). The intense nuclear polarisation (exceeding by several factors of ten and sometimes hundreds the equilibrium polarisation) constitutes unambiguous evidence for the involvement in its generation of unpaired electrons and observation of the effects of nuclear polarisation constitutes a reliable criterion of the existence of radical stages in the reaction. To illustrate CINP, Fig. 1 presents the NMR spectra of the products obtained in the thermal decomposition of benzoyl and acetyl benzoyl peroxides, the spectra were recorded during the reaction.

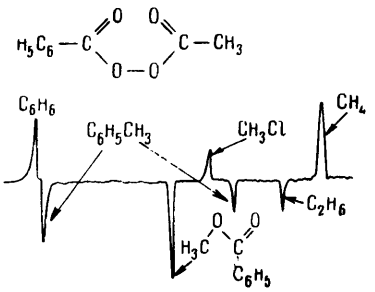
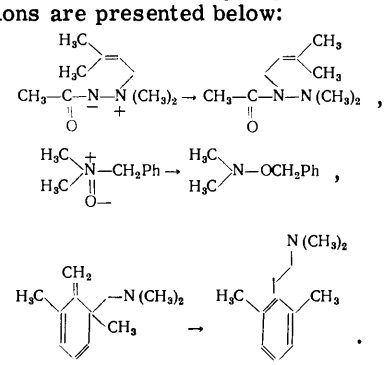


Figure 1. NMR spectrum of products with polarised nuclei in the decomposition of acetyl benzoyl peroxide at 100°C in tetrachloroethylene.

CINP was first observed by Fischer and coworkers[1] in the decomposition of benzoyl peroxide in cyclohexanone when instead of the expected benzene absorption signal an emission signal was noted.

At the present time CINP has been observed and investigated in numerous thermal decomposition reactions of peroxides and azo-compounds[1-9], thermal rearrangements of quaternary ammonium salts[10-13] and quaternary amine oxides[14], and other processes involving isomerisation with migration of molecular groups[15-17]. Examples of such reactions are presented below:



† [Usually referred to a Chemically Induced Dynamic Nuclear Polarisation in English (Ed. of Translation)].

In all these cases CINP of the migrating groups in the products was observed.

The reactions of alkyl halides with lithium alkyls have been investigated in greatest detail[18-25]. CINP has been observed in alkanes and olefins produced in the reactions and also in the molecules of alkyl halides; in the latter case CINP is shown in chemical chain reactions of the type $\dot{R} + XR \rightarrow RX + \dot{R}$. These results led to the conclusion that the reactions of alkyl halides with lithium alkyls have a radical mechanism, the first stage of which is probably a one-electron transfer.

CINP in chemical chain reactions has also been observed in the decomposition of peroxides in the presence of alkyl iodides[26], the chain processes being initiated by peroxide radicals.

Recently CINP was found in reactions of organomercury compounds, for example:

$$PhCH_2HgBr + Ph_3CBr \rightarrow PhCH_2CPh_3 + HgBr_2 ,$$

in which not only the protons of the products but also those of the initial triphenylmethyl bromide are polarised[27].

In reactions of a Grignard reagent with alkyl halides, the olefins and saturated hydrocarbons produced by the reaction of the alkyl radicals derived from the initial reaction components are polarised[28]: the observation of CINP in these reactions constitutes sufficient evidence to assume that the first stage is electron transfer from the Grignard reagent to the alkyl bromide[28].

A distinctive example of CINP in redox reactions is the emission by benzene in the reactions of phenyldiazonium salts with electron-donating reagents (alkalis, *p*-phenylenediamine, the phenoxide anion, and others)[29,30]. It is suggested that the reaction proceeds as follows:

$$PhN_2^+ \xrightarrow{D} (Ph\dot{N}_2) \rightarrow \dot{P}h + N_2 \rightarrow \text{benzene}.$$

CINP has also been observed in the products of many chemical reactions. The protons of anthraquinone were polarised in its photolysis[31]; it is postulated that CINP arises in the deactivation of the excited triplet state of the quinone to the singlet state. In the photolysis of benzophenone CINP was observed in the products of "cage" recombination[32]:

$$Ph_2CO \xrightarrow{h\nu} Ph_2CO^* + HR \rightarrow (Ph_2\dot{C}(OH)\ \dot{R}) \rightarrow Ph_2C(OH)-R .$$

In the photolysis of benzaldehyde, CINP (of the proton in the aldehyde group) was observed in addition to that of the products of the cage recombination of the above kind; it is believed that it arises as a result of chain reactions[33].

This brief description shows that the range of "reactions tested for CINP is fairly large. In most cases new, interesting, and frequently unexpected information about the reaction mechanisms, was obtained with the aid of CINP, and new concepts concerning the course of many chemical reactions have appeared and have become firmly established.

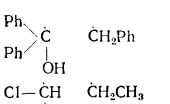
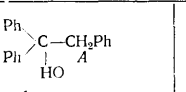
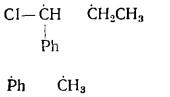
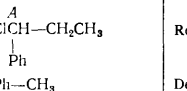
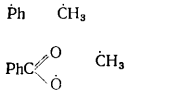
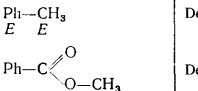
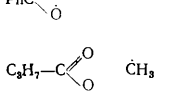
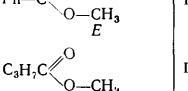
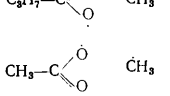
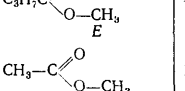
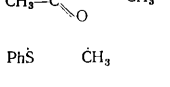
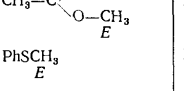
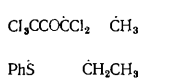
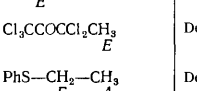
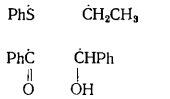
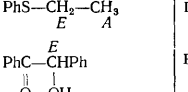
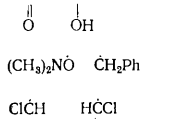
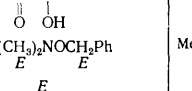
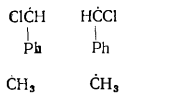
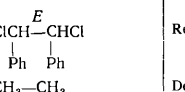
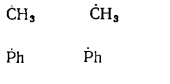
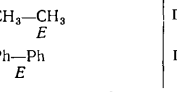
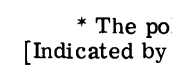
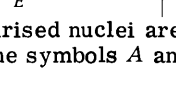
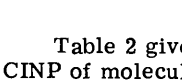
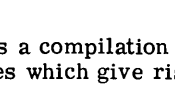
1. Characteristics of the Chemically Induced Polarisation of Hydrogen Nuclei

Reactions in which CINP has been observed are extremely varied. However, analysis of all the results obtained hitherto shows that CINP is determined mainly by the nature of the radical precursers of the product molecules and by the type of the elementary chemical

steps in which the products are formed. On this basis, a fairly simple and complete classification of nuclear polarisations is possible (Tables 1–4).

Tables 1 and 2 show the results on the CINP of the products formed in radical recombination steps. Table 1 summarises those cases where the polarisation of each group of equivalent protons is of the same sign—positive (*A*) or negative (*E*).

Table 1. CINP in recombination reactions (integral polarisation)*.

Recombining radicals	Product and sign of CINP	Reaction and conditions	References
		Photolysis of benzophenone, from triplet pair	32
		Reaction of $PhCHCl_2$ with LiC_2H_5	25
		Decomposition of peroxides	9
		Decomposition of peroxides	9
		Decomposition of peroxides	6
		Decomposition of peroxides	3
		Decomposition of peroxides	3
		Decomposition of peroxides	3
		Decomposition of peroxides	3
		Photolysis of aldehyde	33
		Meisenheimer rearrangement	14
		Reaction of $PhCHCl_2$ with LiC_2H_5	25
		Decomposition of peroxides	3,6,9
		Decomposition of peroxides	9

* The polarised nuclei are indicated in italics [Indicated by the symbols *A* and *E* (Ed. of Translation)].

Table 2 gives a compilation of the results for the CINP of molecules which give rise to NMR spectra with a multiplet structure. The spin multiplets in such molecules exhibit unusual behaviour, of a kind never observed before: the components of the multiplets in high and low fields correspond to polarisation of different signs. Thus the sign of the polarisation of any one group of equivalent nuclei depends on the spin state of another group of nuclei with which the observed group is involved in spin–spin coupling. Fig. 2 illustrates this unusual behaviour of multiplets in CINP, which has been called the multiplet effect (ME). The symbol *A/E* in Table 2 implies that the components at low field correspond to positive polarisation and those at high field to negative polarisation; the symbol *E/A* denotes the opposite situation. The multiplet effect is a property of CINP only and constitutes one of its most remarkable and distinctive features.

Table 2. CINP in recombination reactions (multiplet polarisation).

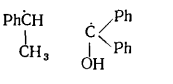
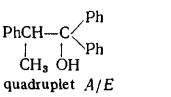
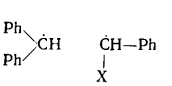
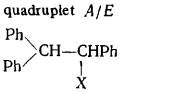
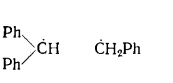
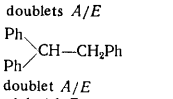
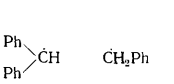
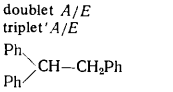
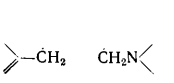
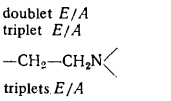
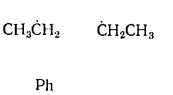
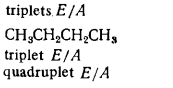
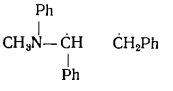
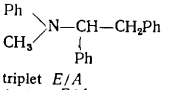
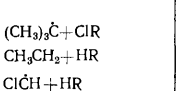
Recombining radicals	Product and sign of CINP	Reaction and conditions	References
	 quadruplet *A/E*	Photolysis of benzophenone, from triplet pair	32
	 doublets *A/E*	Photolysis of diphenyldiazomethane, from triplet pair	35
	 doublet *A/E* triplet *A/E*	Photolysis of diphenyldiazomethane, from triplet pair	35
	 doublet *E/A* triplet *E/A*	Photolysis of diphenyldiazomethane, from singlet pair	35
	 triplets *E/A*	Thermal isomerisation	15
	 triplet *E/A* quadruplet *E/A*	Decomposition of peroxides, reactions of LiC_2H_5 with C_2H_5I	3,21–23
	 triplet *E/A* doublet *E/A*	Isomerisation	20

Table 3. CINP in scission reactions (integral polarisation).

Reaction	Product and sign of CINP	Reaction and conditions	References
$\dot{C}H_3+HR$	CH_4, *A*	Decomposition of peroxides	3,6,9
$\dot{C}H_3+ClR$	CH_3Cl, *A*	Decomposition of peroxides	3,6,9
$(CH_3)_3\dot{C}+HR$	$\underset{E}{(CH_3)_3CH}$	Decomposition of peroxides	3
$(CH_3)_3\dot{C}+ClR$	$(CH_3)_3CCl$, *E*	Decomposition of peroxides	3
$CH_3\dot{C}H_2+HR$	CH_3CH_3, *E*	Decomposition of peroxides	3
	$\underset{A}{PhCH_2Cl}$	Reaction of $PhCHCl_2$ with LiC_2H_5	25
$\dot{P}h+HR$	PhH, *E*	Decomposition of benzoyl peroxide	1,4,5
$\dot{P}h+HR$	PhH, *A*	Decomposition of acetyl benzoyl peroxide	9

As in recombination reactions, the products of abstraction reactions exhibit CINP of two types—integral and multiplet. Table 3 presents the results for the CINP in the products of the abstraction of H, Cl, etc. atoms. Here the polarisation of each group of equivalent nuclei is of one sign. It is interesting to note the behaviour of the methyl radical: it gives rise to negative polarisation in the recombination products and to positive polarisation in the products of abstraction reactions.

Thus the sign of CINP depends on the type of elementary chemical reaction from which the product is formed. Attention should also be drawn to the fact that the sign of CINP is positive for radicals with a negative hyperfine coupling constant ($\dot{C}H_3$, PhH_2) and negative for the $(CH_3)_3\dot{C}$ radical, which has a positive hyperfine coupling constant.

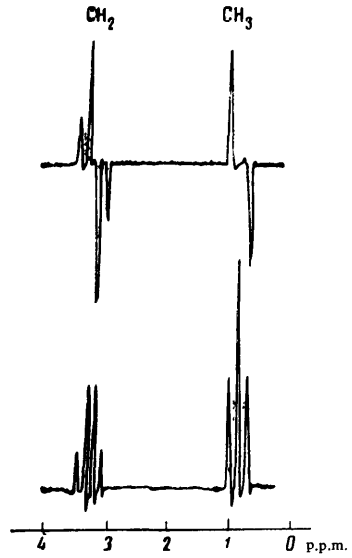


Figure 2. NMR spectrum of ethyl iodide with polarised nuclei in the reaction of ethyl lithium with alkyl iodides (the multiplet effect).

In the phenyl radical mainly the *ortho*-protons are polarised (in relation to the localised unpaired electron); the hyperfine coupling with these protons is in fact a maximum. This conclusion was based on analysis of CINP in the decomposition products of chloro-derivatives of benzoyl peroxide[8]. Trozzolo did not observe the CINP of pentadeuterobenzene in the decomposition of the fully deuterated benzoyl peroxide[8]; on this basis, it was concluded that the nucleus of the hydrogen atom transferred to the phenyl group is not polarised. The difference in the signs of the CINP of benzene in the decomposition of benzoyl and acetyl benzoyl peroxides is very remarkable (Table 3).

Table 4 summarises the results for the CINP of the products of abstraction reactions with a multiplet effect. The following relation governs the multiplet effect in abstraction reactions; a multiplet effect of type A/E is observed in the products, while in the reactants consumed (particularly in chemical relay reactions) the sign of the multiplet effect is reversed to E/A; a theoretical interpretation of these phenomena will be given below.

We may note that the sign of the multiplet effect as well as the sign of the integral polarisation depends on the type of reaction involving the formation of the product. Thus in ethyl chloride the multiplet effect has a sign corresponding to A/E, in butane to E/A, and in thiophenetole CH_3CH_2SPh (Table 1) the multiplet effect is completely absent, although the formation of all these products involves an ethyl radical.

In olefins produced by the disproportionation of radicals a multiplet effect is also observed; for example, the multiplet effect in propene is presented in Fig. 3.

Table 4. CINP in scission reactions (multiplet polarisation).

Reaction	Product and sign of CINP	Reaction and conditions	References
$CH_3\dot{C}H_2+ClR$	CH_3CH_2Cl A/E A/E	Decomposition of peroxides	3
$CH_3\dot{C}H_2+ICH_2CH_3$	CH_3-CH_2I A/E	Reaction of LiC_2H_5 with C_2H_5I	21, 22
$CH_3\dot{C}H_2+ICH_2CH_3$	CH_3-CH_2I E/A E/A	Decomposition of peroxides, chemical chain reaction	26
$(CH_3)_2\dot{C}H+ICH(CH_3)_2$	$(CH_3)_2CHI$ E/A E/A	Decomposition of peroxides, chemical chain reaction	26
$R\dot{C}H_2+ICH(CH_3)_2$	RCH_2I A/E	Decomposition of peroxides chemical chain reaction	26
$CH_3CH_2\dot{C}H_2+ClR$	$CH_3CH_2-CH_2Cl$ A/E A/E	Decomposition of peroxides	3
$CH_3CH_2\dot{C}H_2+IR$	$CH_3-CH_2-CH_2I$ A/E	Reaction of RI with LiR	20—24
$(CH_3)_2\dot{C}H+HR$	$CH_3CH_2-CH_3$ E/A E/A	Decomposition of peroxides	3
$(CH_3)_2\dot{C}H+ClR$	$(CH_3)_2$ $CHCl$ A/E A/E	Decomposition of peroxides	3
$(CH_3)_2\dot{C}H+IR$	$(CH_3)_2$ CHI E/A E/A	Reaction of RI with LiR, chemical chain reaction	22—24
$(\dot{C}H_3)_3C+HR$	$(CH_3)_3$ CH A/E	Decomposition of peroxides, Grignard reaction	26, 28
$CH_3CH_2\dot{C}HCH_3+IR$	$CH_3CH_2CHICH_3$ E/A	Reaction of RI with LiR, chemical chain reaction	24

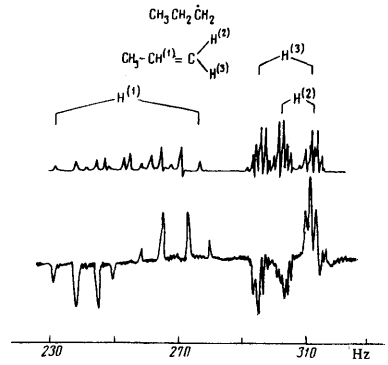


Figure 3. NMR spectrum of propene with polarised nuclei in the reaction of n-propyl iodide with butyl lithium.

The multiplet effect is of type E/A and in the spin multiplet of the proton $H^{(1)}$ only the outer doublet, corresponding to the $\alpha\alpha$ (negative polarisation of $H^{(1)}$) and $\beta\beta$ (positive polarisation of $H^{(1)}$) states of the $H^{(2)}$ and $H^{(3)}$ nuclei, is polarised. (The J_{12} and J_{13} coupling constants are positive). CINP of this type implies that the states $\beta\alpha\alpha$ and $\alpha\beta\beta$ are mainly populated in the molecules (in the series of the spin functions of $H^{(1)}$, $H^{(2)}$, and $H^{(3)}$). It is interesting that the nature of CINP in propene is independent of whether the propene is formed from the $CH_3CH_2\dot{C}H_2$

radical or from $CH_3\dot{C}HCH_3$. The nature of CINP in other olefins (butene, isobutene, etc.) is the same as in propene.

CINP has a number of surprising properties, which are not shown by the usual dynamic nuclear polarisation with radiofrequency pumping at the ESR frequency (see below). The multiplet effect and the dependence of the sign of the multiplet effect and the integral polarisation on the type of chemical reaction are two distinctive features of CINP.

2. The Magnitude of Chemically Induced Nuclear Polarisation.

A third remarkable feature of CINP is the large enhancement factor, greatly exceeding the limiting enhancement attainable in nuclear polarisation with radiofrequency pumping.

We shall now define the enhancement factor E of CINP in terms of the following equivalent relations:

$$E = \frac{M}{M_0} = \frac{I}{I_0} , \qquad (1)$$

where M is the nuclear magnetisation, I the NMR signal, and M_0 and I_0 are their equilibrium values. The value of E shows by what factor the nuclear magnetisation of the molecule exceeds the equilibrium Boltzmann magnetisation. The factor E is an important characteristic of CINP, which is necessary for the verification and experimental tests of any hypotheses and theories of CINP; its determination should be part of the study of CINP in any reaction.

It follows from the definition of E that the kinetics of CINP are associated, firstly, with the kinetics of the chemical reaction and, secondly, with the kinetics of the relaxation processes in the electronic and nuclear spin systems. The establishment of such a relation is of interest for a number of reasons: firstly, in order to be able to use CINP as a method for investigating the kinetics and mechanisms of chemical reactions; secondly, for predicting the kinetic reaction conditions necessary for the maximum development of the CINP expected in the given reactions; thirdly, for the investigation of the physical and chemical mechanisms of CINP.

In the general case the kinetics of CINP in any reaction are described by the equation[36,37]

$$\frac{dM}{dt} = E\frac{dM_0}{dt} - \beta(M - M_0) . \qquad (2)$$

Its first term determines the rate of accumulation of polarisation and is related to the kinetics of the reaction via dM_0/dt, the second term determines the rate of nuclear depolarisation, and $\beta = T_{1n}^{-1}$.

In principle, it is possible to solve Eqn. (2) for any kinetic reaction conditions. The simplest solution is obtained for first-order reactions of the type $A \xrightarrow{k} P$ (for example, decomposition, rearrangement, isomerisation, reactions etc.), when

$$\frac{dM_0}{dt} = \mu_n p_{n0} k A_0 e^{-kt} , \qquad (3)$$

where k is a first-order rate constant and μ_n the magnetic moment of the nucleus:

$$p_{n0} = th\frac{h\gamma_n H_0}{2kT} .$$

When condition (3) holds, solution (2) becomes

$$M(t) = \mu_n p_{n_0} A_0\left[\frac{Ek-\beta}{\beta-k}(e^{-kt} - e^{-\beta t}) - (1 - e^{-\beta t})\right] \qquad (4)$$

It is convenient to convert the magnetisation M into the NMR signal I [see Eqn. (1)] and into the experimentally determined effective enhancement factor K:

$$K = \frac{I(t) - I_{0\infty}}{I_{0\infty}} = \frac{Ek-\beta}{\beta-k}(e^{-kt} - e^{-\beta t}) - e^{-\beta t} \qquad (5)$$

(here $I_{0\infty}$ is the equilibrium signal at $t \to \infty$).

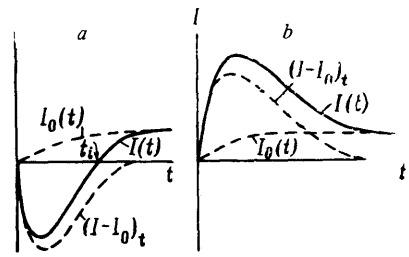


Figure 4. Theoretical CINP kinetic curves; *a*) negative CINP; *b*) positive CINP.

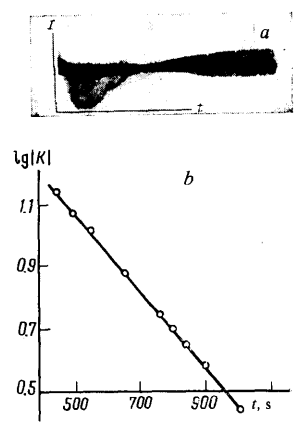


Figure 5. Kinetics of the CINP of protons in the methyl group of methyl benzoate in the decomposition of acetyl benzoyl peroxide: *a*) an experimental record obtained with a rapid scan; *b*) analysis of the kinetics in terms of Eqn. (7).

Fig. 4 presents the theoretical CINP kinetic curves and shows [as was to be expected from Eqn. (5)] that the rate of CINP passes through a maximum. The time required for the attainment of the maximum is

$$t_{max} = \frac{\ln\frac{(E-1)\beta}{Ek-\beta}}{\beta-k} . \qquad (6)$$

In the specific but very common case of fairly slow reactions ($k \ll \beta$), Eqn. (5) is

$$K = (EkT_{1n} - 1)e^{-kt} . \quad (7)$$

Fig. 5 presents an example of experimental CINP kinetics; the satisfactory agreement with the theoretical curve (Fig. 4) is evident. Fig. 5 also presents an analysis of CIPN kinetics on the basis of Eqn. (7); k and E can be immediately determined from a plot of lg $|K|$ against t.

In many cases it is convenient to saturate or invert the NMR signal during the course of the reaction by radiofrequency pulses[38]. This leads to a simplification of the initial kinetic equation (2). Thus at saturation $M - M_0 = 0$ and it is then easy to show that

$$E = \frac{(dI/dt)_{t \to t'}}{I_{\infty} k e^{-kt'}} . \quad (8)$$

Here t' is the instant of saturation (or signal inversion) and $(dI/dt)_{t \to t'}$ is the initial rate of recovery of the CINP signal after saturation (or inversion) (Fig. 6). It is significant that this method does not require a knowledge of the quantity ... [part of Russian text missing (Ed. of Translation)].

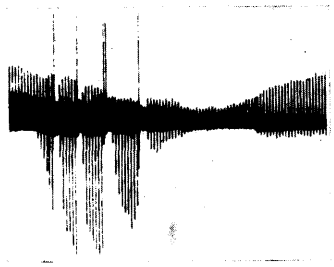
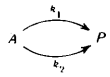


Figure 6. CINP kinetics with signal inversion by radiofrequency pulses.

In chemical kinetics situations very frequently arise where the same substance is formed by different pathways, some of which have a radical mechanism and lead to CINP, while others are non-radical and are not accompanied by CINP. Suppose, for example, that in the scheme



one of the pathways in the conversion of A into P with a constant k_1 leads to CINP, while the other pathway is non-radical.

In this case

$$K = \frac{Ek_1 + k_2 - \beta}{\beta - \Sigma k}(e^{-\Sigma kt} - e^{-\beta t}) - e^{-\beta t} , \quad (9)$$

where $\Sigma k = k_1 + k_2$. If the reaction is slow, i.e. $\Sigma k \ll \beta$, then

$$K = (Ek_1T_{1n} + k_2T_{1n} - 1)e^{-\Sigma kt} . \quad (10)$$

Using Eqns. (9) and (10) it is possible, in principle, to decide whether there really is a competition between radical and non-radical mechanisms and also to determine their kinetic parameters.

The CINP kinetics and their relation with the kinetics of chemical reactions have been considered in greatest detail by Buchachenko[39], who also examined various kinetic situations (consecutive and competing reactions, bimolecular reactions, etc.).

Eqn. (2) postulates, of course, that the product formed in the reaction, containing polarised nuclei, is not consumed in other reactions, is not precipitated, does not evaporate, etc. However, these conditions frequently break down and this must be borne in mind in the calculation of the factor E.

In particular, a method has been proposed[40] for the determination of E for a volatile product (a gas: methane, CO_2, etc.).

Finally, equations have been presented[36] for the kinetics of nuclear polarisation when, together with chemically induced polarisation, there is also radiofrequency pumping at the ESR frequency of the radicals involved in the reaction.

Table 5. Enhancement factors for CINP.

Molecule*	Type of CINP	Sign and magnitude of CINP**	References
C_6H_6	Integral	$-(80 \pm 10)$	42
CH_4	Ditto	$+10^3$	39
PhC(=O)OCH_3	»	$-(1600 \pm 100)$	42
CH_3—OC(=O)—$OCH(CH_3)_2$	»	$-(800 \pm 200)$	42
Ph, Ph C—CH_2Ph, OH	»	$+(250 \pm 25)$	32
Ph, Ph CH—CH_2Ph	A/E	$\pm(760 \pm 100)$ for $m_{CH_2} = \pm 1$	35
Ph, Ph C—CH—Ph, OH, CH_3	A/E	$\pm(1300 \pm 200)$ for $m_{CH_3} = \pm 1/2$	32

* Polarised protons are designated by italic symbols.

** The enhancement factors were calculated per group of equivalent nuclei.

It is noteworthy that all the kinetic equations presented for the determination of E are independent of the mechanism of nuclear polarisation: E refers to a molecule or to a group of equivalent nuclei in the molecule. All the known values of E for CINP are listed in Table 5.

We may note that for integral polarisation the factor E in most cases greatly exceeds the maximum enhancement factors in nuclear polarisation with radiofrequency pumping (−330 for dipole relaxation and +660 for scalar relaxation[41]).

The factors E for multiplet CINP are also high. For example, for the proton in the CH group (last row of Table 5) the quadruplet lines with $m_{CH_3} = \pm\frac{1}{2}$ (inner lines) correspond to a polarisation of $\pm(1300 \pm 200)$.

The kinetic equations for CINP permit the use of such polarisation as a new kinetic method for the investigation of chemical reaction mechanisms, i.e. as a

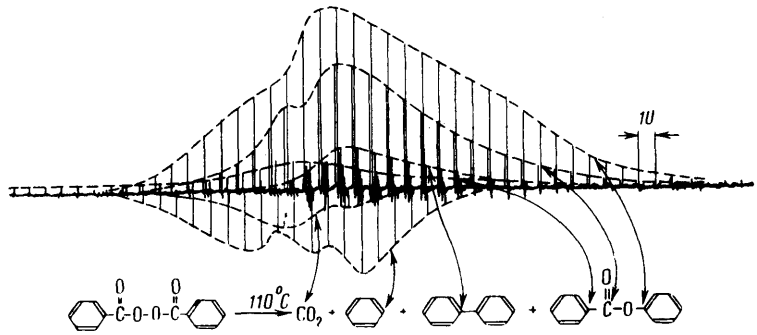


Figure 7. Kinetics of the chemically induced polarisation of ^{13}C nuclei in the decomposition of benzoyl peroxide in cyclohexanone at 110°C (proton signal saturated).

method for the determination of the rate constants and nuclear polarisation factors E. We may note that these equations are independent of the physical mechanism of CINP, since the physical information is contained in the factor E. The experimental determination of these factors and their relation with the lifetime of radicals and other experimental conditions (magnetic field strength, temperature, viscosity, the presence of radical acceptors, etc.) are important for the elucidation of the physical mechanism of CINP.

3. Chemically Induced Polarisation of ^{19}F, ^{13}C, and ^{31}P Nuclei

Tables 1–5 present the results for the chemically induced polarisation of protons. In a series of recent investigations, CINP of many-electron atoms was also observed. Fischer and coworkers[2] discovered the positive polarisation of ^{19}F in the decomposition of benzoyl peroxide in *p*-fluorobenzaldehyde and *p*-fluorostyrene. It was suggested that in the first case nuclear polarisation is induced chemically in the reaction products of aldehyde radicals of the type $-\dot{C}=O$ and in the second in the products of addition to styrene (polymerisation products). However, detailed studies on the nature of the products with CINP were not made.

Rakshys[43] observed chemically induced polarisation of ^{19}F nuclei in a fluoro-derivative of dibenzyl and in pentylbenzene (fluorine was successively substituted in the aromatic rings in the *ortho*-, *meta*-, and *para*-positions). These products were obtained by the reaction of fluorine-substituted benzyl fluoride with n-butyl-lithium. In contrast to the previous investigation, here chemically induced polarisation of ^{19}F nuclei exhibits a strong multiplet effect, which is fairly complex, so that it is difficult to interpret it unambiguously from the NMR spectra.

Chemically induced polarisation of ^{13}C nuclei forming part of the skeleton of organic molecules is of greatest interest. It was first observed[44] in the decomposition of benzoyl and acetyl benzoyl peroxides. Fig. 7 presents the kinetics of the chemically induced polarisation and the assignments of the polarised ^{13}C nuclei in the molecules. The chemically induced polarisations of ^{13}C and H nuclei are compared in Table 6. The differences in sign are discussed below.

It is remarkable that the carbonyl carbon atoms in the phenyl ester of benzoic acid and in carbon dioxide are polarised with different signs (Fig. 7) although both products are formed from the benzoyloxy-radical. Saturation of ^1H NMR (heteronuclear double resonance) does not influence the chemically induced polarisation of ^{13}C nuclei; the latter is[45] about 10^4 and, like chemically induced polarisation of protons, greatly exceeds the polarisation with radiofrequency pumping.

Table 6. Signs of the chemically induced polarisation of protons and ^{13}C nuclei.

Molecule	Group of atoms	Sign of CINP	
		protons	^{13}C
CH_4	CH_4	*A*	*E*
$Ph-C(=O)-O-CH_3$	CH_3	*E*	*A*
$Ph-CH_3$		*E*(*ortho*)	*A*(*ortho*)
	CH_3	*E*	*A*
		E	*E*

We may note finally that a recent communication[46] reports the observation of chemically induced polarisation of ^{13}P nuclei in various reactions involving phosphites, phosphates, and peroxides. The polarisation exhibits an extremely wide variety of signs and values but it is difficult to give a sufficiently reliable and unambiguous interpretation in these reactions owing to their complexity.

III. THEORY AND MECHANISM OF CHEMICALLY INDUCED NUCLEAR POLARISATION

The simplest mechanism of CINP depends on the Overhauser effect in free radicals during their lifetime—from the instant of generation to the instant of their conversion into diamagnetic products. This mechanism of CINP was in fact proposed in the early investigations[1,19].

We shall now examine the Overhauser effect in qualitative terms. Consider the simplest electronic-nuclear system consisting of one electron and one proton: its Zeeman levels are shown schematically in Fig. 8. If there is magnetic coupling between the unpaired electrons and the proton (isotropic or dipolar) in such a system, then in principle there exist four types of relaxation processes between the Zeeman electronic and nuclear levels: (1) purely electronic transitions when the magnetic quantum number of the electron M changes but the nuclear spin quantum number m does not; these are $\Delta M = \pm 1$ and $\Delta m = 0$ vertical transitions corresponding to ESR; (2) purely nuclear transitions--$\Delta M = 0$ and $\Delta m = \pm 1$ horizontal transitions (NMR transitions); (3) $\Delta M = \Delta m = \pm 1$ flip-flop transitions; (4) $\Delta M = -\Delta m = \pm 1$ flip-flop transitions. In the last two transitions there is simultaneous flipping of the spins of the electron and of the nucleus in the same or in the opposite directions; there is at the same time a change in the population of the Zeeman levels of the electronic and nuclear spin systems[47].

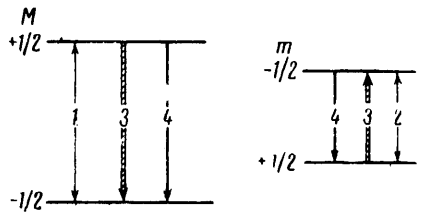


Figure 8. A schematic representation of the Zeeman levels and transitions in an electron–nucleus system with a spin of 1/2.

Usually in the observation of nuclear polarisation two frequencies are used: one for the saturation of the vertical transitions (ESR) and for the equalisation of the populations of the electron levels and the other for the detection of changes in the populations of the nuclear Zeeman levels (NMR). After the removal of the saturating field at the ESR frequency, the electronic Zeeman system tends to return to equilibrium, corresponding to the Boltzmann distribution of electron spins among the Zeeman levels. Then processes (1) are accompanied by transitions (4), in which there is an increase in the population of the lowest nuclear level (positive polarisation), and transitions (3), which increase the population of the highest nuclear level and can actually lead to inversion of the populations (negative polarisation). Positive polarisation predominates when the main contributions to relaxation come from isotropic hyperfine coupling and negative polarisation predominates when dipolar coupling is dominant. Negative polarisation is usually employed in radiofrequency masers[47].

In principle, nuclear polarisation may be induced by a chemical reaction and not radiofrequency pumping of the electronic levels. If the chemical reaction involves the formation of radicals, it may happen that the electronic Zeeman levels will have equal populations or, in the general case, non-equilibrium populations. Next a Boltzmann distribution of the populations of the electronic levels is established in the radical with an electronic relaxation time T_{1e} and a new population of nuclear levels (polarisation of nuclei) arises owing to transitions (3) and (4). If the radical is further converted into a molecule (by a chemical reaction) nuclear polarisation appears in the product molecule and is detected in it. It is then necessary that the lifetime of the radical τ_R should be longer than or comparable to T_{1e}, i.e. that there is sufficient time for the occurrence of the relaxation processes (3) and (4). However, τ_R must not be too long so that the nuclear polarisation can be transferred to the molecule before disappearing in the radical with a nuclear relaxation time $T_{1n}^{(R)}$. Thus $T_1 \ll \tau_R < T_{1n}^{(R)}$, or

$10^{-7}-10^{-6}$ s $< \tau_R < 10^{-4}-10^{-5}$ s.

Within the framework of the above mechanism, chemically induced polarisation differs from the usual polarisation only by the method of pumping to electronic Zeeman levels. If this mechanism of CINP is valid, there should be three main consequences.

1) The sign of the nuclear polarisation of the radical and hence the sign of the CINP of the product molecules into which it is converted is predictable on the basis of its chemical structure. Thus the radical $\dot{C}H_3$ should have negative polarisation, while in the $CH_3\dot{C}H_2$ radical one may expect positive polarisation of the protons in CH_3 and negative polarisation of the protons in CH_2, etc.

2) The products derived from the radicals should exhibit the polarisation established in the radicals and its sign should be determined solely by the nature of the radical and should be independent of its origin, of its further reactions, and of the nature of the product formed.

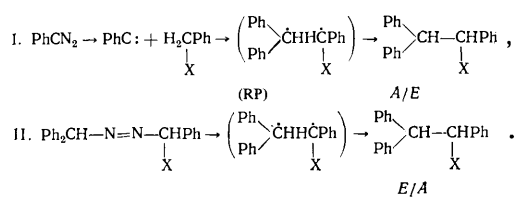
3) The magnitude of CINP should not exceed –330 for dipolar electronic-nuclear relaxation in the radical and +660 for scalar relaxation.

The three main characteristics of CINP formulated in the preceding section quite unambiguously contradict these conclusions. This implies that the mechanism of CINP based on the simple Overhauser effect cannot account for its characteristics and the relations which it exhibits. One must assume that elementary chemical steps involved in the generation and destruction of radicals are responsible for CINP and therefore the mechanism of such polarisation should be sought in the chemical steps.

1. Theory and Mechanisms of Chemically Induced Nuclear Polarisation Involving $S-T_0$ Transitions.

The concepts concerning the mechanisms of CINP arose from simple and elegant experiments by Closs and coworkers[48,49], in which the same products were obtained in different ways and CINP was observed in them. An example of the preparation of the same product in different ways is presented below. Pathway I consists of the decomposition (photochemical or thermal) of diphenyldiazomethane; this yields diphenylcarbene, which has a triplet ground state. One may assume that, regardless of the state in which the carbene is generated, during its lifetime it passes to the ground state and reacts in the triplet state, abstracting a hydrogen atom from a neighbouring molecule in the solution. This results in the formation of a radical pair (RP) in the triplet state, which can subsequently give rise to either recombination products (for this, a preliminary triplet–singlet transition in

the radical pair is necessary) or the radical pair can dissociate into individual radicals, which are released into the bulk phase:



Pathway II consists of the dissociation of the azo-compound accompanied by the liberation of a nitrogen molecule and the formation of the same radical pair as in the first case but only in the singlet state. Recombination of radicals with the radical pair yields the same product as in the first case.

Thus in the first case the precursor of the final reaction product is the radical pair in the triplet state and in the second case the radical pair in the singlet state. Different types of CINP in the final product correspond to the different spin multiplicities of the precursor: in the first case the multiplet effect in the CH−CH group corresponds to A/E and in the second to E/A.

Hence one can immediately conclude that a possible mechanism of CINP is a selection of nuclear-spin states in the radical pairs (precursors of the products) as a result of singlet−triplet transitions.

We shall now consider briefly the simplest theories of CINP based on $S-T$ transitions[48-52] in radical pairs. Suppose that we have the radical pair

$$(H\dot{R}_1\dot{R}_2) \begin{cases} \nearrow HR_1{-}R_2 \text{ (recombination)} \\ \searrow H\dot{R}_1 + \dot{R}_2 \text{ (radical pair dissociation),} \end{cases}$$

which can either recombine or dissociate: suppose further that the radical pairs liberated participate in substitution reactions (for example, they abstract atoms from solvent molecules, becoming thereby converted into stable products).

We shall now calculate the probabilities of the transfer to the recombination products of an $H\dot{R}_1$ proton with a spin α_n and β_n. We shall consider the singlet state of the pair with the wave function $S = 1/\sqrt{2}(\alpha\beta - \beta\alpha)$ and the triplet state $T_0 = 1/\sqrt{2}(\alpha\beta + \beta\alpha)$ (other triplet states, T_{+1} and T_{-1}, will be disregarded at present, since they are separated from the S and T_0 levels by the energy of the electronic Zeeman interaction).

The complete wave functions of the pair consist of the combination of the states S and T_0:

$$\begin{aligned} \psi^+(t) &= [c_S^+(t)\,S + c_{T_0}^+(t)\,T_0]\,\alpha_n\,, \\ \psi^-(t) &= [c_S^-(t)\,S + c_{T_0}^-(t)\,T_0]\,\beta_n\,; \end{aligned} \qquad (11)$$

$c_S^{\pm}(t)$ and $c_{T_0}^{\pm}(t)$ determine the proportions of the states and the superscripts + and − refer to states with nuclear spins α_n and β_n respectively.

Suppose that the pair is initially in a triplet state, i.e. $|c_S^{\pm}(0)|^2 = 0$ and $|c_{T_0}^{\pm}(0)|^2 = 1$. The problem is to find the evolution of the triplet wave function in the system to the singlet wave function under the influence of the perturbing Hamiltonian:

$$\mathcal{H} = \beta H_0(g_1S_1 + g_2S_2) - JS_1S_2 + aIS_1\,. \qquad (12)$$

Here the first term describes the energy of the Zeeman interaction (g_1 and g_2 are the g-factors of the radicals in the pair), the second term is the exchange energy operator, and the third term describes the hyperfine interaction.

The exchange interaction in the pair alters as a result of fluctuations in the geometry of and the distances in the pair under the influence of thermal motion in the liquid; the mixing of the S and T_0 states takes place as a result of the difference between the Zeeman energy $(g_1 - g_2)\,\beta H_0$ and the hyperfine coupling energy.

The result of operation using the Hamiltonian (12) may be obtained by solving the Schrödinger equation for the coefficients $c_S^{\pm}(t)$ and $c_{T_0}^{\pm}(t)$. Then

$$\begin{aligned} c_S^{\pm}(t) &= -i\frac{{}^1/_2\beta H_0\Delta g \pm {}^1/_4 a}{D^{\pm}}\sin D^{\pm}t\,, \\ c_{T_0}^{\pm}(t) &= \cos D^{\pm}t - \frac{iJ}{D^{\pm}}\sin D^{\pm}t\,, \end{aligned} \qquad (13)$$

where $D^{\pm} = [({}^1/_2\beta H_0\Delta g \pm {}^1/_4 a)^2 + J^2]^{1/2}$.

The probability of the formation of the recombination product from the triplet pair at time τ is equal to the proportion of the S state $|c_S^{\pm}(\tau)|^2$ at this instant:

$$|c_S^{\pm}(t)|^2 = \frac{{}^1/_2\Delta g\beta H_0 \pm {}^1/_4 a}{(D^{\pm})^2}\sin^2 D^{\pm}\tau\,. \qquad (14)$$

By averaging over the lifetime of the radical pair, we finally obtain the rates of population of the nuclear-spin states in the recombination product:

$$w^{\pm} = k_0\frac{2\,(1/2\,\Delta g\beta H_0 \pm 1/4\,a)^2\tau^2}{1 + 4\,(D^{\pm})^2\tau^2}\,, \qquad (15)$$

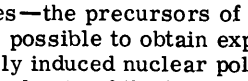
where k_0 is the overall rate of formation of the radical pair and τ is its lifetime.

It follows from Eqn. (15) that the rates of formation of molecules with hydrogen spins α_n and β_n are proportional to $(\Delta g\beta H_0 + {}^1/_2 a)^2$ and $(\Delta g\beta H_0 - {}^1/_2 a)^2$ respectively. Clearly the probabilities of observing the α or β spins of the proton in the molecule formed on recombination of the radical pair are different and depend on the magnitude and sign of $\Delta g = g_1 - g_2$ and the hyperfine coupling constants. Thus, when $\Delta g < 0$ and $a < 0$, we have $w^+ > w^-$, i.e. positive polarisation obtains in the recombination product from the triplet pair, while the radicals liberated from the radical pair and converted into other products in the bulk phase are negatively polarised.

If the initial pairs are in the singlet state, then $w^- > w^+$ since pairs with an α spin are more rapidly converted into the triplet state and then dissociate. In this case the recombination products are depleted in α spins and an excess of β spins remains, i.e. the polarisation is negative; positive polarisation now appears in the reaction products of the free radicals.

Thus for specified values and signs of a and Δg, the sign of CINP depends on the spin multiplicity of the radicals in the pair and hence on the spin multiplicity of the reacting species—the precursors of the radical pair.

Similarly it is possible to obtain expressions for the multiplet chemically induced nuclear polarisation by considering a radical pair of the type



The rates of population of different nuclear-spin states or the rates of $S-T_0$ transitions are proportional to

the squares of matrix elements of the type $\langle S|\mathcal{H}|T_0\rangle$ calculated with the Hamiltonians

$$\mathcal{H}_{\mathrm{I}} = \beta H_0(g_1S_1 + g_2S_2) - JS_1S_2 + a_1S_1I_1 + a_2S_2I_2\ , \quad (16)$$

$$\mathcal{H}_{\mathrm{II}} = \beta H_0(g_1S_1 + g_2S_2) - JS_1S_2 + (a_1I_1 + a_2I_2)S_2\ , \quad (17)$$

for pairs of types I and II respectively.

Table 7. Relative rates of $S-T_0$ transitions.

Nuclear-spin states	Pair (I)	Pair (II)
$\alpha_n\alpha_n$	$(\Delta g\beta H_0/2+a_1/4+a_2/4)^2$	$(\Delta g\beta H_0/2+a_1/4-a_2/4)^2$
$\alpha_n\beta_n$	$(\Delta g\beta H_0/2+a_1/4-a_2/4)^2$	$(\Delta g\beta H_0/2+a_1/4+a_2/4)^2$
$\beta_n\alpha_n$	$(\Delta g\beta H_0/2-a_1/4+a_2/4)^2$	$(\Delta g\beta H_0/2-a_1/4-a_2/4)^2$
$\beta_n\beta_n$	$(\Delta g\beta H_0/2-a_1/4-a_2/4)^2$	$(\Delta g\beta H_0/2-a_1/4+a_2/4)^2$

Table 7 lists the relative rates of population of various states of a system of two nuclei (protons) in the recombination product.

For example, when $a_1 < 0$ and $a_2 < 0$ and the initial type I radical pair is in the triplet state, the populations of the nuclear-spin states $\alpha_n\alpha_n$ and $\beta_n\beta_n$ in the recombination product $\diagdown$CH−CH$\diagup$ increase and the $\alpha_n\beta_n$ and $\beta_n\alpha_n$ states become depleted. This leads to the appearance of chemically induced nuclear polarisation with an A/E multiplet effect (the populations and polarisations are illustrated schematically in Fig. 9). A multiplet effect of this type was in fact observed by Closs[48] in the decomposition of diphenyldiazomethane. Clearly the sign of the multiplet effect in the reaction products of the radicals liberated from the radical pair is opposite to that of the multiplet effect in the recombination products, since the nuclear states $\alpha_n\beta_n$ and $\beta_n\alpha_n$ in the liberated radicals become enriched.

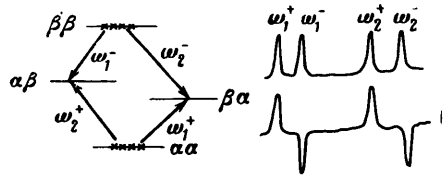


Figure 9. Schematic representation of multiplet CINP in the $\diagdown$CH−CH$\diagup$ molecular fragment from a triplet radical pair.

Within the framework of the theory of chemically induced nuclear polarisation involving $S-T_0$ transitions in radical pairs, it is possible to predict the signs of the integral CINP and of the multiplet effect as a function of the signs of Δg and a; these results are summarised in Tables 8 and 9.

It is now possible to make a number of generalisations concerning CINP.

1. The integral polarisation and the multiplet effect in the products of the recombination of the radicals in pairs and of the reactions of free individual radicals should have opposite signs.

Table 8. Integral CINP in recombination products.

Multiplicity of radical pair	$\Delta g<0,\ a<0$ $\Delta g>0,\ a>0$	$\Delta g<0,\ a>0$ $\Delta g>0,\ a<0$
Singlet	*E*	*A*
Triplet	*A*	*E*

A—positive polarisation (absorption).
E—negative polarisation (emission).

2. If $\Delta g = 0$ in the pair, only multiplet CINP should be observed, its value being proportional to a^2; if $\Delta g \neq 0$, integral CINP proportional to $\Delta g\beta H_0 a$ should be observed. Frequently both types of CINP may be observed.
3. The signs of the integral CINP and of the multiplet effect depend on those of Δg and a (as shown in Tables 8 and 9) and also on the type of radical pairs [(I) or (II)] and their spin multiplicity.

Table 9. Multiplet CINP in recombination products.

Multiplicity of radical pair	Pair (I)		Pair (II)	
	$a_1<0,\ a_2<0$	$a_1<0,\ a_2>0$	$a_1<0,\ a_2<0$	$a_1<0,\ a_2>0$
Singlet	*E/A*	*A/E*	*A/E*	*E/A*
Triplet	*A/E*	*E/A*	*E/A*	*A/E*

Extensive experimental data have now been obtained in various laboratories, which makes it possible to verify the consequences and characteristics of CINP formulated above. It was found that in the vast majority of cases the experimental data are consistent with these consequences, i.e. at least in the region of high fields (of the order of several thousand gauss) the mechanism based on $S-T_0$ transitions in radical pairs generates CINP fairly effectively and gives a correct qualitative description of its characteristics.

2. Analysis of the Mechanisms of Chemical Reactions from the Standpoint of Chemically Induced Nuclear Polarisation

We shall now consider the significance of CINP for chemistry and chemical physics.

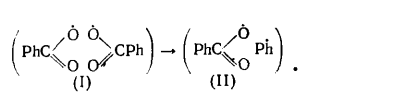
1. In the first place the very fact of the observation of CINP indicates the presence of radical stages in the reaction, i.e. the involvement in the reaction of intermediate paramagnetic species—ions or radicals. In this sense detection of CINP has become a new and powerful method for the investigation of the mechanisms of chemical reactions.

2. The appearance in chemical reactions of CINP with the properties described above implies that the reactions involve the formation of radical pairs. It is also possible to determine whether the g-factors of the radicals differ, whether there is hyperfine coupling, and the type of the radicals in the pair [(I) or (II)]. Moreover, at the present time CINP is used with increasing frequency as a quantitative method for the determination of the g-factors of the radicals in the pair (or their differences) and also the values and signs of the hyperfine coupling constants.
3. When the values of a and Δg for the radicals in the pair are known, it is possible to determine from the signs of the integral CINP and of the multiplet effect the spin multiplicity of the radical pairs (precursors of the products) and hence the spin multiplicity of the reacting species generating the radical pairs. Analysis of CINP shows that thermal and photochemical decomposition reactions of peroxides and azo-compounds take place in the singlet state and that the primary radical pairs are in this state. Singlet pairs are also formed in thermal rearrangement and isomerism reactions, in the Wurtz and Grignard reactions, and others. Photochemical decomposition of peroxides sensitised by ketones and also thermal decomposition of diazo-compounds take place with formation of primary triplet pairs. The multiplicity of the reacting species is an extremely important characteristic of the reaction mechanism and this information is carried by CINP.

Above (see p. 808) it was shown how Closs and coworkers obtained the same products from singlet and triplet radical pairs. The third method consisted in an independent generation of the same radicals as separate species, new radical pairs with so called non-correlated spins being subsequently generated in the encounters between these radicals in solution. Since the S and T_0 states are being produced statistically in the same way, one may assume that CINP should not be observed in the products from such secondary radicals of pairs (the CINP in the singlet and triplet pairs should mutually cancel out). However, experiments showed that the recombination products from secondary pairs exhibit the CINP characteristic of triplet pairs[52]. This implies that the lifetime of the triplet pairs is longer than that of the singlet pairs and consequently the steady-state concentration of the triplet pairs in solution is higher than that of the singlet pairs. This is an important and non-trivial result for the dynamics of chemical reactions.
5. It follows from the previous two conclusions that the products obtained from primary radical pairs and those generated from secondary radical pairs, i.e. from pairs of freely colliding radicals, may be resolved. This permits a deeper and more detailed understanding of the chemistry of the processes, i.e. the mechanisms of the chemical reactions.

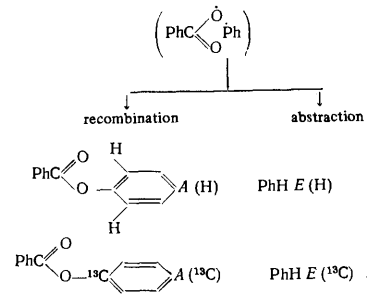
We shall now consider the mechanisms of a number of reactions from the standpoint of CINP.

The decomposition of benzoyl peroxide takes place with formation of a radical pair:



(I) (II)

The radical pair (I) can be either converted into (II) or can recombine with formation of the initial molecule. Such recombination is well known from experiments involving the transfer of an ^{18}O tracer from the carbonyl to the ester group[53]. However, neither H nor ^{13}C nuclei show CINP, since $\Delta g = 0$ in pair (I). In pair (II) $\Delta g \neq 0$ and CINP should obtain in its reaction products:



In the phenyl radical $a_{^{13}C} > 0$, $a_{H(ortho)} > 0$, and $g_{PhCOO} > g_{Ph}$ and consequently the signs of the chemically induced polarisation of the H and ^{13}C nuclei in the recombination products correspond to recombination in a singlet pair (Table 8). In benzene formed from the liberated radicals the CINP is of the opposite sign, as predicted by the theory.

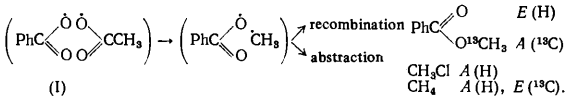
There is reason to believe that $a_{^{13}C} < 0$ ($\rho^{\pi}_{^{13}C} < 0$, as in the allyl fragment) in the $Ph^{13}C(=O)O\cdot$ radical, so that the ^{13}C nucleus in the product of the recombination of this radical with the phenyl radical in pair (II) should exhibit positive chemically induced polarisation if pair (II) is in the singlet state. This prediction is found to be valid (Fig. 7). Moreover, in the radicals $Ph^{13}C(=O)O\cdot$ liberated from the pair ^{13}C should be negatively polarised and, in the decarboxylation of these radicals, the CO_2 molecules should be negatively polarised; this prediction is also fulfilled (Fig. 7).

Thus the signs of the chemically induced polarisation of the H and ^{13}C nuclei in the principal thermal decomposition products of benzoyl peroxide show that the decomposition takes place in the singlet state. The same signs are observed in direct photolysis and photochemical decomposition sensitised by aromatic hydrocarbons, which implies that the decomposition in this case proceeds via excited singlet states. In the photochemical decomposition sensitised by ketones having the energy of the lowest triplet level (>56 kcal mole^{-1}), the signs of CINP in the decomposition products are reversed (for instance benzene protons are positively polarised and the *ortho*-protons of the phenoxy-ring in phenyl benzoate are negatively polarised). This implies that the decomposition of the peroxide in the presence of ketones proceeds via the triplet state[54,55].

We may note that, according to theory, chemically induced polarisation of the nuclei in the adjacent carbon atoms of the two benzene rings of biphenyl should have the same sign as in benzene if both these products are obtained from phenyl radicals liberated from the primary singlet pair (II). In fact the sign of the chemically induced polarisation of the ^{13}C nucleus in biphenyl is opposite to that of the ^{13}C nucleus in benzene. This implies that benzene is mainly obtained directly from the radicals liberated from the pairs, whereas biphenyl is obtained from radicals which had sufficient time after

liberation from the primary pair to be involved in collisions with other radicals of the type $PhC(=O)O\cdot$. In such secondary pairs with non-correlated electron spins CINP of the same sign as in triplet pairs is generated. Thus the "short-lived" phenyl radicals are converted into benzene and the "long-lived" radicals participate in secondary collisions and yield biphenyl with chemically induced polarisation of ^{13}C nuclei of the opposite sign.

Acetyl benzoyl peroxide is decomposed by the same mechanism:



(I)

Evidently the signs of CINP in the CH_3 group of the recombination products correspond to their formation from a singlet pair (see Table 8; $\Delta g < 0$, $a_H < 0$, and $a_{^{13}C} > 0$).

CINP in the reaction products of radicals liberated from pair II has the opposite sign (in agreement with theory). It is interesting that, as for biphenyl, the ethane formed in the decomposition of benzoyl peroxide is negatively polarised (in contrast to methane). This implies that methane (and CH_3Cl) are formed from the "short-lived" methyl radicals, whereas ethane is formed mainly from the "long-lived" radicals involved in secondary (triplet) collisions in which they acquire negative polarisation.

We shall now consider the mechanism of the reactions of secondary radicals generated in the decomposition of benzoyl peroxide in the presence of various additives. Fischer and coworkers investigated CINP in the decomposition of benzoyl peroxide in the presence of a mixture of molecules of different types (RX and R'X'); the free radicals $\dot{R}$ and $\dot{R}'$ appeared in the system independently under these conditions [56]. The signs of CINP in the asymmetric recombination products R–R' corresponded to the case where the same products were produced from triplet pairs. This implies that the recombination of independently generated radicals takes place in the pairs with non-correlated spins (in agreement with the results of Closs and coworkers [52]; (see p. 808 above).

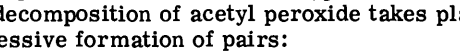
The signs of CINP in the reaction products of radicals liberated from asymmetric pairs (i.e. in R'R', RR, R'X, and RX') are opposite to those of CINP in the asymmetric recombination products (as would be expected from the theory of CINP with $S-T_0$ transitions).

Rykov et al. [34] investigated the decomposition of benzoyl peroxide in the presence of methyl iodide. Here $\dot{C}H_3$ radicals were generated independently and it might have been expected that in the CH_3 group of methyl benzoate and in methane the signs of CINP should correspond to *A* and *E* respectively (as in the products formed from pairs with non-correlated spins). In fact it was found that the signs of CINP in these products correspond to *E* and *A*, i.e. as in the products from singlet pairs. In order to account for this effect, one may assume that the radicals $PhC(=O)O\cdot$ (or $\dot{P}h$) react with CH_3I in the primary pair (I) or (II); this involves the immediate formation of the singlet secondary pair ($PhC(=O)O\cdot\ CH_3$) resembling pair (II) in the decomposition of acetyl benzoyl peroxide.

CINP of the CH_3 protons in methyl benzoate and in methane arises in this secondary pair. CINP in ethane and in the CH_3 group of toluene is negative, which is consistent with the formation of these products from the "long-lived" CH_3 radicals, i.e. from pairs with non-correlated spins.

The hypothesis that the primary pair is immediately converted into a secondary pair is equivalent to the hypothesis of a comparatively high reactivity of radicals in the primary pairs. Subsequently we shall consider other examples consistent with this hypothesis.

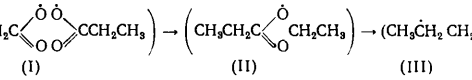
The decomposition of acetyl peroxide takes place with successive formation of pairs:



(I) (II) (III)

In the OCH_3 group of methyl acetate and in CH_4 (or CH_3Cl) the signs of CINP correspond to *E* and *A* respectively; this implies that these products are formed mainly from the singlet pairs (II). However, in the products of the recombination of CH_3 with solvent radicals ($PhSCH_3$ in thiophenol and $CH_3-CCl_2COCCl_3$ in hexachloroacetone), the signs of CINP of the CH_3 groups should be positive, since these products should be formed from pairs with non-correlated spins (random collisions). In fact the signs of CINP of these products are negative (as in singlet pairs). Thus here too one must assume that the radicals in the primary pairs exhibit an enhanced reactivity and therefore the primary pairs are rapidly converted into secondary singlet pairs of the type ($\dot{C}H_3$ $\dot{S}Ph$) or ($\dot{C}H_3$ $\dot{C}Cl_2COCCl_3$). CINP of ethane is negative. Its origin can be explained if it is assumed that the ethane is formed from the pair (III) and the polarisation in the latter persists from the preceding pair. Possibly this is also the explanation of the CINP of biphenyl formed from benzoyl peroxide.

The decomposition of propionyl peroxide is interesting:



(I) (II) (III)

The decomposition proceeds via singlet pairs, because in butane the sign of the multiplet effect corresponds to *E/A* and in CH_3CH_2Cl [the reaction products of the $CH_3\dot{C}H_2$ radical liberated from the pair (II) or (III)] the multiplet effect has the opposite sign (corresponding to *A/E*). In the photochemical decomposition of this peroxide sensitised by ketones the signs of the CINP of these products are reversed [54], which implies that the decomposition proceeds via an excited triplet state.

$PhS-CH_2CH_3$ with CINP of the CH_2 (*E*) and CH_3 (*A*) groups is formed in the decomposition of propionyl peroxide. The signs of CINP correspond to the formation of this product from the singlet pair ($\Delta g < 0$, $a_{CH_2} < 0$, $a_{CH_3} > 0$) and not from pairs with non-correlated spins as would have been expected. Thus here too one must assume that the primary singlet pairs are rapidly converted into secondary pairs, i.e. the reactivity of the radicals in the primary pairs is enhanced, so that their reactions in the pair successfully compete with the liberation of the radicals from the pair by diffusion.

We shall now consider CINP in chemical chain reactions. The iodide $CH_3(CH_2)_9CH_2I$ with an *A/E* multiplet effect is formed in the decomposition of undecyl peroxide $[CH_3(CH_2)_9CH_2COO]_2$ in the presence of ethyl iodide [26]. This corresponds to the liberation into the bulk phase of the radical $CH_3(CH_2)_9\dot{C}H_2$ from the primary singlet pair.

At the same time $CH_3\dot{C}H_2$ is generated and is in turn transformed by a chemical chain reaction into ethyl iodide with an E/A multiplet effect. This sign of the multiplet effect arises in radicals liberated from pairs with non-correlated spins. Thus ethyl radicals produced in the decomposition of the peroxide undergo random collisions and form pairs with non-correlated spins. On liberation from such pairs, they acquire multiplet E/A CINP and, on being converted into ethyl iodide, transfer this polarisation to the molecule of the latter.

This mechanism accounts for the previously mentioned (p. 804) characteristics of CINP in chain reactions: the signs of the multiplet effect in the products formed and in the reactants consumed (iodides) are opposed. The explanation is that the products are generated from singlet pairs and CINP in the reactants arises in radical pairs with non-correlated spins.

The CINP of the iodides formed and consumed in Wurtz reactions can be explained in the same way. Thus, in the reaction of CH_3CH_2Li with $(CH_3)_2CHI$, ethyl iodide has a multiplet effect with the sign corresponding to A/E and isopropyl iodide has the sign corresponding to E/A. Other examples are presented in Table 4.

It is interesting that in the reaction of ethyl-lithium with ethyl iodide both radicals are identical and the opposite signs of the multiplet effects in the ethyl iodide molecules consumed and formed should cancel out. In fact a multiplet effect with the sign corresponding to A/E is observed, which implies that the CINP of ethyl iodide formed from the primary singlet pair predominates.

Analysis of the CINP of the products of the Wurtz reaction, thermal isomerisation, and rearrangements shows that the products are formed mainly from primary pairs on disproportionation or recombination and their CINP is generated in the primary pairs. The results for CINP show that, as in the thermal decomposition of peroxides, the primary pairs in the Wurtz and thermal isomerisation reactions are in the singlet state.

3. Mechanisms of the Chemically Induced Nuclear Polarisation Involving $S-T_{-1}$ Transitions.

The behaviour of the singlet and triplet levels in molecules dissociating into radicals (or conversely in a pair of recombining radicals) is shown in Fig. 10. The above mechanism of CINP in radical pairs involving $S-T_0$ transitions postulates that the distances R between the radicals in the radical pair are fairly large, i.e. one considers radical pairs beyond the point of intersection of the S and T_{-1} levels when the S and T_0 levels converge closely and the T_{-1} levels are separated by the Zeeman interaction energy. In $S-T_0$ transitions the nuclear spins are not inverted and there is only a selection, i.e. sorting of the radicals with respect to nuclear spins, some of which, with a specific orientation of the nuclei, pass to the recombination products, while others, with the opposite orientation of the nuclei, are liberated into the bulk phase and are converted into other molecules. $S-T_0$ transitions are induced by changes in the exchange energy J in fluctuations of the distances in the radical pairs and are due to the secular component of the hyperfine coupling. Thus in $S-T_0$ transitions the elementary chemical step itself does not give rise to polarisation. However, CINP can be generated also by another mechanism, namely one involving $S-T_{-1}$ transitions which are due to the non-secular component of the hyperfine coupling, $\mathcal{H}_{\text{non-sec}} = \frac{1}{2}a\,(I_+S_- + I_-S_+)$, and which are accompanied by a reorientation of the nuclear spins in the recombination or dissociation step.

The $S-T_{-1}$ transition should be particularly effective at the quasi-intersection point of these levels (Fig. 10). The point is at $R \simeq 3-4$ Å‡.

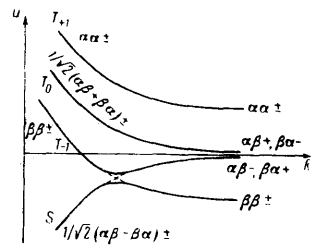


Figure 10. Behaviour of energy levels in the radical pair.

Fig. 10 shows on the left the states of molecules or radical pairs and on the right the states formed non-adiabatically (i.e. when the point of intersection is rapidly traversed). If the motion along the levels takes place slowly and adiabatically, then, for example in dissociation in the singlet state, the matrix elements $\langle\alpha\beta^-|\mathcal{H}_{\text{non-sec}}|\beta\beta^+\rangle$ are not zero and consequently triplet pairs will be enriched in the $\beta\beta^+$ states and singlet pairs will be depleted in the $\alpha\beta^-$ states. This implies that in the products of the recombination of singlet pairs there will be an excess of nuclear spins with negative polarisation and in the radicals liberated from triplet pairs there will be positive polarisation. Clearly in this case the reaction plays an active role in the generation of CINP, since the nuclei are reoriented in the elementary chemical recombination steps itself.

According to this mechanism, the sign of CINP should be independent of the signs of a and Δg (in contrast to the mechanism involving $S-T_0$ transitions). These features make it possible to distinguish these two mechanisms. Analysis of the experimental data shows that in high fields the mechanism with $S-T_0$ transitions mainly operates. This means that the dissociation and recombination processes take place non-adiabatically, i.e. the point of intersection of the levels is traversed rapidly and apparently only once. This conclusion is important for the understanding of the physical mechanisms of chemical processes.

Evidently in weak fields (of the order of tens or hundreds of gauss when the Zeeman interaction is comparable to the hyperfine interaction) the point of intersection of the levels is displaced to the region where $R \simeq 6-8$ Å; clearly in this region the contributions of $S-T_{-1}$ transitions to the generation of CINP will increase appreciably owing to the repeated traversing of the point of intersection in the fluctuations of the geometry of the radical pair. In general, in weak fields all $S-T$ transitions will contribute to CINP.

‡ This quantity may be estimated from the approximate relation $J \simeq J_0 e^{-\alpha R}$, where J_0 is the exchange integral corresponding to the bond energy, J is of the order of magnitude of the energy of the Zeeman interaction, and $\alpha \simeq 1$ Å^{-1}.

This is also indicated by the behaviour of the sign of CINP as a function of field strength. Thus, it has been shown[9,57] that in the decomposition of benzoyl peroxide benzene protons are positively polarised in weak fields. This polarisation increases with field strength to a maximum at 20 G and then falls, reaching zero at about 100 G. When $H_0 > 100$ G, CINP becomes negative. A change in the sign of CINP as a function of the field has also been observed in many other investigations. In all these cases the reaction was performed in weak fields (outside the magnetic field of the NMR spectrometer) and the specimen was then rapidly transferred to the NMR transducer of the spectrometer and CINP generated in weak fields was detected in high fields. In one study[5] the reaction (decomposition of benzoyl peroxide) was carried out and CINP was detected in fields of 30–47 G. The observed CINP was negative, but this result does not contradict other data[8,57], since in NMR detection in weak fields the overall NMR signal of all kinds of protons is observed and one cannot rule out the possibility that the main contribution to the NMR signal comes from the negative CINP of products other than benzene.

The next step in the theory of CINP will probably consist in a correct allowance for all the transitions in radical pairs and the calculation of their probabilities. In chemical kinetics, the solution of this problem will yield information about the states and interactions in radical pairs, about the dynamics of the motion of radicals in the pair, and about the probability of the recombination or collision of the radicals.

4. Chemically Induced Nuclear Polarisation in Atom Transfer Steps

The CINP of products of substitution reactions (or atom transfer reactions) has the same properties as in recombination (Tables 3 and 4). The mechanisms of CINP were examined in the preceding Sections. They are based on the hypothesis of $S-T$ transitions in the radical pairs, the dissociation of which gives rise to free radicals with polarised nuclei. These mechanisms have received reliable experimental confirmation.

However, the problem of whether CINP can be generated in elementary atom transfer steps and whether there are mechanisms capable of generating CINP in such steps is significant. The idea that CINP can arise in atom transfer steps was put forward by Rykov et al.[34] It arose from the following experimental finding: in the decomposition of peroxides in carbon tetrachloride, chloroform with negative CINP is detected. It was postulated that this polarisation arises in the steps involving the abstraction of hydrogen atoms by $\dot{C}Cl_3$ radicals from solvent molecules. However, this evidence is not unambiguous; CINP could arise in chloroform owing to the disproportionation of radicals in radical pairs by the mechanism discussed above (p. 809).

We have seen that in recombination reactions selection with respect to states takes place in triplet–singlet transitions. By analogy with recombination, the involvement of excited states in atom transfer steps can also be postulated. Such an analogy was drawn by Gerhart and Osterman[58].

The transition state in the transfer reaction $\dot{R} + XR' \rightarrow RX + \dot{R}'$ is regarded formally as a set of three radicals ($\dot{R}X\dot{R}'$) in the doublet state. As in the recombination reactions, the mixing of multiplet states owing to hyperfine coupling is considered and by analogy only the secular component of the isotropic hyperfine coupling is taken into account as a perturbation and the non-secular component and dipole–dipole interactions of the radical spins are neglected. The starting point in this treatment is the concept of a symmetrical wave function (s) of the transition state. Next follows the hypothesis that the decomposition of the state (activated complex) into the final products is facilitated by the mixing of the symmetrical (s) and antisymmetric (a) states owing to isotropic hyperfine coupling. Such mixing leads to the preferential population of levels with a minimum overall projection of nuclear spins (as in the recombination steps in the singlet state).

The introduction of antisymmetric spin states is equivalent to allowance for the excited states of the activated complex (by analogy with $S-T$ transitions in radical pairs in recombination). This hypothesis has evident consequences for CINP.

1. In the product RX of the reaction $R + XR' \rightarrow RX + \dot{R}'$ the states with the minimum overall projection of nuclear spins will be more populated and therefore in R'X these states will be depleted. This implies that the signs of the multiplet effect will be opposed and will correspond to A/E in RX and to E/A in R'X. This behaviour does indeed obtain (see Table 4 and the relevant comments).
2. The sign of the multiplet effect can also change when the direction of the reaction alters, i.e. the reaction $R + XR' \rightarrow \dot{R}X + R'$ is transformed into $\dot{R}' + XR \rightarrow R'X + \dot{R}$. This corollary has not been tested directly.
3. If R' = R, the multiplet CINP should be zero. This corollary hardly ever holds.
4. The enhancement factor E should depend on the nuclear spin in the multiplet because the probabilities of the transitions between the symmetrical and antisymmetrical states in the activated complex depend on the hyperfine interaction energy.

Despite the apparent confirmation of the idea of transitions between symmetrical (s) and antisymmetric (a) states there are two arguments which give rise to serious doubts about the validity of this mechanism.

Firstly, $s-a$ transitions are considered only in the step involving the decomposition of the activated complex. However, reverse transitions of the same type should occur in the formation of the activated complex, which should apparently lead to the cancellation of CINP in the atom transfer step.

Secondly, the magnitude of CINP should depend on the difference Δ between the energies of the s and a states and should be defined by the approximate relation $E \simeq a/\Delta$. Since $a \simeq 10^8-10^9$ s^{-1} and $E \simeq 10^3$, it follows that $\Delta \simeq 10^{11}-10^{12}$ s^{-1}. Thus, to be effective, the mechanism of CINP invoking excited states of the activated complex must involve the mutual approach of the ground and excited levels to within an energy of the order of a vibrational quantum. It is unlikely that such a situation can be realised; the real energy is of the order of one electron-volt.

Thus CINP in atom transfer steps can hardly be explained by invoking excited states of the activated complex. The problem of the intrinsic mechanisms of CINP in steps involving the transfer of atoms from the molecule to the radical remains open.

IV. CHEMICALLY INDUCED ELECTRONIC POLARISATION

Chemically induced electronic polarisation (CIEP) is revealed in the ESR spectra of atoms and radicals.

As in CINP, the polarisation of electrons is of two types - multiplet and integral. CIEP was observed for the first time by Fessenden and Schuler[59] in the ESR spectrum of hydrogen atoms in the radiolysis of liquid hydrocarbons: the low field component of the doublet corresponded to emission and the high field component corresponded to strong absorption. The hyperfine coupling constant for the hydrogen atom is positive and therefore the above spectrum implies that the hydrogen atoms are generated predominantly in the $\alpha\alpha_n$ and $\beta\beta_n$ spin states (the first symbol denotes the spin function of the electron and the second of the proton; the α-electron is oriented along the field and occupies the upper Zeeman level, because $\gamma_e < 0$). The $\alpha\alpha_n$ states give rise to an emission spectrum and the $\beta\beta_n$ states to an absorption spectrum (multiplet effect of type E/A). An analogous spectrum with multiplet polarisation was obtained for deuterium atoms[59].

Initially this effect was not understood; an attempt was made to attribute it to the technical conditions in the observation of ESR (modulation amplitude and phase, level of microwave power, etc.). However, five years after the publication of the paper of Fessenden and Schuler[59] a similar multiplet effect was observed by Smaller et al.[60] in the ESR spectra of radicals in the pulse radiolysis of liquid hydrocarbons. Thus all the low field components of the ESR spectrum of cyclopentyl radicals with $m_\alpha = \pm\frac{1}{2}$ and $m_\beta > 0$ corresponded to emission and all the high field components with $m_\alpha = \pm\frac{1}{2}$ and $m_\beta < 0$ corresponded to absorption (m_α and m_β are the quantum numbers of the projections of the nuclear spins of the α- and β-hydrogen atoms in the radical). Since the hyperfine coupling constant for β-protons is positive, such a spectrum corresponds to exactly to the same population of the electronic-nuclear spin levels as in hydrogen and deuterium atoms: the electron with an α-spin "escapes" to nuclei with α-spins and the electron with a β-spin "escapes" to nuclei with β-spins. One may postulate that, for a negative hyperfine coupling constant, the $\alpha\beta_n$ and $\beta\alpha_n$ states will be populated preferentially.

It was also shown[60] that the multiplet ESR spectrum is converted into the usual spectrum over a period of several microseconds. The kinetics of the variation of the emission signal from one of the hyperfine components are presented in Fig. 11. As in CINP (p. 805) a polarisation maximum is observed; the electronic relaxation times may be determined from the rate of depolarisation: they vary in the range 6–60 μs and depend on m_β, i.e. on the hyperfine interaction energy.

The problem of the mechanism of the multiplet polarisation of electrons will now be considered. If radicals are formed in the dissociation of molecules, all the processes occurring under these conditions can be treated as in recombination, i.e. the concept of $S-T$ transitions in dissociating radical pairs may be invoked (by analogy with the previous treatment of CINP in terms of recombining pairs). Then $S-T_0$ transitions will lead to multiplet CIEP, while $S-T_{\pm1}$ transitions can give rise to appreciable integral CIEP; in this case there is clearly a complete analogy with the mechanisms of CINP in recombination products.

The difference consists in the model adopted to describe the motion along the dissociation reaction coordinate. We shall consider as an example a study by Fischer[61], in which it was postulated that motion along the reaction coordinate is so slow that the S and T_0 states vary adiabatically. The spin-Hamiltonian for a pair of radicals is of the usual type:

$$\mathcal{H} = g\beta H_0(S'+S) - {}^1/_2 J(1+4\,SS') + h\Sigma a I_z S_z + h\Sigma a' I'_z S'_z .$$

Within the framework of the approximation employed, the problem reduces to the solution of a quadratic equation and for adiabatic conditions we obtain

$$\psi^+ = \frac{1}{\sqrt{2}}(AS + BT_0); \qquad (18)$$

$$\psi^- = \frac{1}{\sqrt{2}}(AT_0 - BS); \qquad (19)$$

$$A = \left(1 + \frac{1}{\sqrt{1+x^2}}\right)^{1/2}; \; B = \frac{x}{|x|}\left(1 - \frac{1}{\sqrt{1+x^2}}\right)^{1/2};$$

$$S = \frac{1}{\sqrt{2}}(|\alpha\beta m_1 m_{1'}\rangle - |\beta\alpha m_1 m_{1'}\rangle); \qquad T_0 = \frac{1}{\sqrt{2}}(|\alpha\beta m_1 m_{1'}\rangle + |\beta\alpha m_1 m_{1'}\rangle);$$

$$x = \frac{\Sigma a m_I - \Sigma a' m_{I'}}{2|J|}; \; J = J_0 e^{-t/\tau} .$$

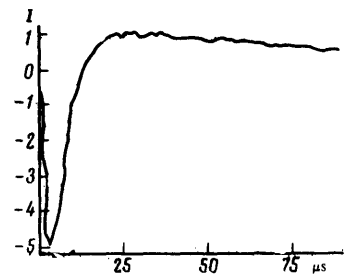


Figure 11. Kinetics of the variation of the amplitude of the component with $m_\beta = +1$ and $m_\alpha = -1/2$ in the ESR spectrum of cyclopentyl radicals.

Next it is postulated that at a certain instant $t = \tau'$ there is an instantaneous breakdown of the radical pair, which leads either to decomposition into free radicals, or to recombination, or transfer reactions. Since these processes are assumed to be fast (in the sense that they do not involve a change in the population of the magnetic states), the resulting populations are calculated by a simple projection of Eqns. (18) and (19) on to the relevant states of free radicals or molecules. Thus we have the following relative populations of the states of radicals in the decomposition of a singlet molecule:

$$a_{\alpha\alpha m_1 m_{1'}} = 0; \qquad a_{\alpha\beta m_1 m_{1'}} = {}^1/_4(A+B)^2; \qquad a_{\beta\alpha m_1 m_{1'}} = {}^1/_4(A-B)^2;$$

$$a_{\beta\beta m_1 m_{1'}} = 0; \; J = J_0 e^{-\tau'/\tau} .$$

These populations explain qualitatively the multiplet polarisation of electrons. The value of Fischer's work consists in the fact that he clearly formulated the principal reason for the change in the populations of the magnetic states in the dissociation step. This consists in the fact that the conditions which obtain for motion along the dissociation reaction coordinate are adiabatic.

However, an important comment must be made concerning the calculation itself. The point is that the redistribution of populations takes place mainly in the region where $J \simeq a$, i.e. when the traversal is never adiabatic. On the other hand, the applicability of

adiabatic conditions, discussed by Fischer refers to the region where $J \gg a$, which should not apparently make a significant contribution to chemically induced polarisation of nuclei and electrons.

A somewhat different dissociation model was considered by Kaptein and Oosterhoff[62]. Suppose that a molecule HX dissociates via the mechanism

$$H{-}X \rightarrow (\dot{H}\ \dot{X}) \rightarrow \dot{H} + \dot{X}$$

and one has to calculate the probability of the population of the levels of the hydrogen atom formed. The Hamiltonian for the pair is of the form

$$\mathcal{H} = \omega_e (S_1^z + S_2^z) - JS_1S_2 + a(S_1^z + S_2^z) I^z .$$

Here the non-secular terms are neglected and only the $T_0 - S$ transitions are considered (as for CINP, p. 809). It is postulated that in the dissociation J falls sharply to a value of the order of a, the pair remains in the singlet state, and subsequently dissociates with formation of an H atom in one of the states. (We may note that these are in fact the same approximations as those employed by Voss to account for the multiplet CINP in recombination products). Suppose that the nuclear spin is α_n; then the state of the radical pair is described by the wave function

$$\varphi^+(t) = [c_S(t)\, S + c_{T_0}(t)\, T_0]\alpha_n .$$

On substituting this function into the time dependent Schrödinger equation, we obtain a set of equations for the coefficients $c_S(t)$ and $c_{T_0}(t)$:

$$i\dot{c}_S = Jc_S + Ac_{T_0} ,$$
$$i\dot{c}_{T_0} = Ac_S - Jc_{T_0} ,$$

where $A = \frac{1}{4}a$. After finding the coefficients for the boundary conditions $c_S(0) = 1$ and $c_{T_0}(0) = 0$, we have

$$\varphi^+(t) = [\cos \omega t S - i\omega^{-1} \sin \omega t (JS + AT_0)]\alpha_n ,$$

and for the wave function with a nuclear spin β we have

$$\varphi^-(t) = [\cos \omega t S - i\omega^{-1} \sin \omega t (JS - AT_0)]\beta_n ,$$

where $\omega = (A^2 + J^2)^{1/2}$. Now the (oscillating) spin density at the H atom may be calculated:

$$\rho^{\pm} = 2\langle \varphi^{\pm}(t) | S_1^z \delta(r_1) | + S_2^z \delta(r_2) | \varphi^{\pm}(t) \rangle = \pm 2AJ\omega^{-2} \sin^2 \omega t .$$

This equation shows that the electron with a nuclear spin α has a higher density at the α nucleus.

If the spin density is now averaged over the lifetime of the pair $(\dot{H}\ \dot{X})$, we obtain the selectivity parameter

$$\delta^{\pm} = \frac{1}{\tau} \int_0^{\infty} \rho^{\pm}(t) e^{-t/\tau} dt = \pm \frac{4AJ\tau^2}{1 + 4\omega^2\tau^2} .$$

The rates of population of the levels in the H atom are

$$\alpha\alpha_n\ {}^1/_4 k(1 + \delta^+), \qquad \beta\alpha_n\ {}^1/_4 k(1 - \delta^+),$$
$$\alpha\beta_n\ {}^1/_4 k(1 + \delta^-), \qquad \beta\beta_n\ {}^1/_4 k(1 - \delta^-),$$

where k is the rate constant for the formation of the pairs. Evidently the $\alpha\alpha_n$ and $\beta\beta_n$ states are populated preferentially; this leads to a multiplet effect in the ESR spectrum of the hydrogen atom and the multiplet polarisation is proportional to δ and depends on J, a, and τ in the radical pair. Evidently the sign of ME in the ESR spectrum depends on the state in which the atom or radical is formed—the singlet or triplet state (as in CINP).

The multiplet polarisation of electrons has been observed in radicals formed not only in dissociation steps but also in transfer steps. Fischer and coworkers[63] investigated the electron spin resonance of the radicals $\dot{C}H_2CH_2COOH$ and $CH_3\dot{C}HCOOH$ from propionic acid by a flow method in the $Ti^{3+} - H_2O_2$ redox system. As in the work of Smaller et al.[60], the hyperfine coupling components with $m_\alpha = \pm 3/2$ gave rise to emission; other lines with $m_\beta > 0$ were found to have a lower amplitude, since here absorption was partly compensated by emission.

We must now note the following important factor. Since the probabilities of the population of various electronic-nuclear levels of the radical in a chemical reaction are different, one can consider the variation of the rate constant for the chemical reaction with nuclear spin, i.e. with the hyperfine coupling energy in the radicals formed (and possibly also destroyed). Thus the multiplet effects in the chemically induced polarisation of nuclei and electrons can be explained even when the difference between the rate constants amounts to only a few per cent. However, usually the rate constants measured in chemical kinetics are overall quantities averaged over the nuclear-spin states and there is no point in considering their variation with the spin. In other words, the integral rate constants k (see above). are independent of the spin, while the quasidifferential constants $k(1 \pm \delta)$ do depend on the nuclear spin. At present the only method for the measurement of the differential (with respect to the nuclear spin) reaction cross-sections is based on chemically induced polarisation. It would be interesting to attempt to find this type of relation between reaction cross-section and the spin in experiments with magnetically oriented molecular beams (provided that this is possible in principle).

The ESR spectra do not reveal solely multiplet CIEP. Recently reports have appeared[64,65] of the preparation of radicals with a completely inverted population of the Zeeman electronic levels; their ESR spectrum exhibited total emission over a period of several microseconds after preparation and was then converted into the normal ESR absorption spectrum. The radicals were obtained by pulse or continuous illumination of benzophenone, benzaldehyde, 2- and 4-chlorobenzaldehydes, acetophenone, dibenzyl, and anthraquinone by light from a nitrogen gas laser (λ = 3371 Å) or from a mercury lamp.

The causes of the total emission are so far obscure. One can only put forward certain hypotheses. On irradiation, excited triplet states are formed, which on reaction with the solvent form triplet radical pairs. If one of the radicals relaxes rapidly, then, owing to the non-secular component of the exchange interaction $JS_{\pm 1}S_{\mp 2}$, there may be an inversion of population in the second radical (as in the Overhauser effect). It is also possible that some of the triplet excited states (for example T_0 and T_1) are rapidly deactivated; the remaining T_{+1} states react with formation of a T_{+1} pair, which dissociates into radicals with electron spins α. Such selective deactivation of triplets in a magnetic field was observed in a solid on the basis of ESR and phosphorescence spectra[66], but it is not clear whether such a mechanism can operate in a liquid. A mechanism involving $S - T_{-1}$ transitions should also be effective (as in CINP, p. 813).

Finally, we may note that cosmic radiofrequency emission by hydroxyl radicals is also associated with the inverted population of their magnetic-rotational states[67]. This emission comes from regions of ionised gas near young and newly formed stars; such a region with a high concentration of hydroxyl radicals with an inverted population operates as a gigantic cosmic oscillator or

possibly as an amplifier—a celestial maser. Little is known about the mechanisms of inverted population; optical pumping has been mainly considered, but this hypothesis involves many difficulties and therefore one cannot rule out the possibility of chemical pumping[67-70].

V. THE IMPORTANCE AND PROSPECTS OF CHEMICALLY INDUCED NUCLEAR POLARISATION

In order to understand how chemically induced polarisation of electrons and nuclei takes place, it is first necessary to discover how the elementary chemical step occurs, what is its physical mechanism, and what is its physical model. It is already quite clear that many details of elementary chemical reactions may be understood with the aid of chemically induced polarisation of electrons and nuclei. This is in fact why chemically induced polarisation constitutes at present a "hot spot" at the junction of a number of disciplines: theory of the elementary step, magnetic relaxation, radiofrequency spectroscopy, chemical kinetics, and others; this has given rise to much interest in the phenomena of chemically induced polarisation.

Many fundamental problems in the theory of chemically induced polarisation are still obscure. However, what has already been achieved has proved very fruitful. The dual role of elementary chemical reactions is clear in principle: the passive role, consisting in the selection of radicals and molecules with respect to electronic-nuclear and nuclear spin states, and the active role, leading to the induction of polarisation in the elementary steps themselves. Such separation has already significantly aided the solution of the problem. Clearly CINP and CIEP contain information about electron–electron and electron–nucleus interactions in the activated reaction complex, about the time variation of these interactions, about the behaviour of the energy levels in the activated complex, etc. There is no doubt that the development of the theory of chemically induced polarisation will be closely related to the development of the theory of the elementary step.

The role of CINP as a new and powerful research method for the kinetics and mechanisms of chemical reactions must be emphasised; the sensitivity of CINP as a method for the identification of radical stages is higher by several powers of 10 than the sensitivity of the ESR method.

It is significant that CINP is shown not only in the reaction products of alkyl and phenyl radicals, where there is a powerful electron–nucleus magnetic interaction, but also in the reaction products of oxy-radicals where such interaction is weak[6]. This greatly extends the scope of the CINP method. A large-scale application of the CINP method in the study of various chemical reactions is at present of great interest both for the reactions and the method itself. The phenomena of chemically induced polarisation are also of some interest for physicists, since they give rise to new methods for the polarisation of nuclei and electrons.

The fundamental tasks in the field of chemically induced polarisation are, firstly, further development of the qualitative and quantitative theories of the phenomena associated with the theory of the elementary chemical steps and, secondly, a large-scale application of the chemically induced polarisation methods in a wide variety of chemical and biological processes.

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Methods of Synthesis of αω-Difunctional Oligosiloxanes with Two Organic Substituents Per Unit

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The methods of preparation of oligosiloxanes with two organic substituents per unit, containing the functional groups $X(R_2SiO)_nSiR_2X$ (X = Cl, OCOR, OR, NR_2, OH, or ONa) at the terminal silicon atom, have been considered and a critical assessment of the possibility of employing the methods for the synthesis of oligomers with specified n and X has been made.
The bibliography includes 187 references.

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I. INTRODUCTION

Recently organosilicon oligomers containing reactive substituents at the ends of the chain have assumed increasing theoretical and practical interest. These compounds occupy an intermediate position between organosilicon monomers and polymers, which have been thoroughly investigated and widely described in the chemical literature.

The most important application of αω-difunctional organosilicon oligomers is the synthesis of polymers with regular structures. By controlling the sequence of fragments in the main chains of the macromolecules, it is possible to alter sharply the properties of the polymers without affecting or only slightly altering their composition. Condensation of αω-difunctional oligomers with organic and inorganic monomers, organic derivatives of the elements, and also with one another makes it possible to obtain new types of polymers with valuable technical properties. This reaction has already found wide application in the synthesis of organosilicon block polymers, siloxanes with a number of atoms of other elements, and other types of silicon-containing high-molecular-weight compounds.

Organosilicon oligomers can also be used themselves as heat exchangers, stabilisers for rubber mixtures based on organosilicon polymers, etc.

The methods of preparation of αω-difunctional organosilicon oligomers have not so far been adequately treated in monographs on organosilicon chemistry and in reviews. The aim of the present paper is to fill this gap. It deals with the methods of synthesis of αω-difunctional oligosiloxanes which can be isolated in a pure form.

II. METHODS OF SYNTHESIS OF αω-DIHALOGENO-OLIGOSILOXANES

1. Partial Hydrolysis of Chlorosilanes with an Organic Substituent

Hydrolysis of chlorosilanes with an organic substituent is one of the most important reactions in organosilicon chemistry. This reaction makes it possible to convert such chlorosilanes, obtained by direct synthesis from silicon and halogeno-derivatives of hydrocarbons[1-5], directly into siloxane polymers with organic substituents.

Hydrolysis of dichlorosilanes with two organic substituents by an excess of water usually leads to the formation of cyclosiloxanes and only an insignificant amount of linear siloxanes[6-8]. In the presence of a deficiency of water, the principal hydrolysis products are linear oligosiloxanes with chlorine atoms at the ends of the chain. As a rule, hydrolysis yields a mixture of oligomers with various contents of silicon atoms in the molecule:

$$n\,RR'SiCl_2 + (n-1)\,H_2O \rightarrow Cl(RR'SiO)_{n-1}SiRR'Cl + 2(n-1)\,HCl,$$

where $n \geqslant 2$. The hydrolysis is usually carried out in a solvent, sometimes in the presence of a hydrogen chloride acceptor.

Thus αω-dichloro-oligodimethylsiloxanes with the general formula $Cl[(CH_3)_2SiO]_{n-1}Si(CH_3)_2Cl$ are obtained in the hydrolysis of dichlorodimethylsilane with water, the reactants being in molar proportions of 2:1.[9,10] The maximum yields of these oligomers (28% for $n = 2$, 24% for $n = 3$, 15% for $n = 4$, 6% for $n = 5$, 3% for $n = 6$, and 2% for $n > 6$) can be achieved by hydrolysis in a homogeneous medium using a mixture of ether and dioxane as a solvent. Under these conditions, 22% of the initial $(CH_3)_2SiCl_2$ does not react.

In hydrolysis in the absence of a solvent (a two-phase system), the yield of αω-dichloro-oligosiloxane falls and the amount of unreacted dichlorodimethylsilane increases. At the same time octamethylcyclotetrasiloxane (D_4) and decamethylcyclopentasiloxane (D_5) appear in the reaction mixture.

The increase of the content of higher oligomers in the reaction mixture is promoted by a decrease of the $(CH_3)_2SiCl_2:H_2O$ molar ratio from 2 to 1.8–1.5.[11] For the ratio 1.5:1, the yield of oligomers with $n \geqslant 3$ increases by a factor greater than 2.

Hydrolysis of dichlorodimethylsilane or dichloromethylsilane in ether at −70°C yielded αω-dichloro-oligodimethylsiloxanes with $n = 1-3$ [12] or $1-5$ [13] and αω-dichloro-oligomethylsiloxanes $Cl(CH_3SiHO)_nSi(CH_3)HCl$ with $n = 1-4$ [13] respectively.

When a 1 : 18 : 1 (wt.%) mixture of $(CH_3)_3SiCl$, $(CH_3)_2SiCl_2$, and CH_3SiCl_3 was treated with a 62% solution of hydrogen chloride in water under pressure, 1,3-dichlorotetramethyldisiloxane and 1,5-dichlorohexamethyltrisiloxane were obtained in yields of 33.4 and 20.4% respectively[14].

$\alpha\omega$-Dichloro-oligomethylphenylsiloxanes have been obtained by the hydrolysis of dichloromethylphenylsilane with a deficiency of water in the presence of a solvent[15]. Under optimum conditions, the yields of oligomers containing 2, 3, 4, 5, and 6 silicon atoms in the molecule were 32, 25, 7, 4, and 4% respectively; 21% of $CH_3(C_6H_5)SiCl_2$ does not react. The reaction mixture also contains *sym*-trimethyltriphenyl cyclotrisiloxane and *sym*-tetramethyltetraphenylcyclotetrasiloxane.

Hydrolysis without a solvent results in the formation of only 8% of a mixture of distillable oligomers containing 2% of 1,3-dichloro-1,3-dimethyl-1,3-diphenyldisiloxane and 47% of higher $\alpha\omega$-dichloro-oligosiloxanes. The amount of unreacted $CH_3(C_6H_5)SiCl_2$ increases to 45%.

1,3-Dichloro-1-methyl-1,3,3-triphenyldisiloxane was obtained by the simultaneous hydrolysis of dichloromethylphenylsilane and dichlorodiphenylsilane in toluene at 80°C.[16] 1,3-Dichloro-1,3-dimethyl-1,3-diphenyldisiloxane is formed when moist dichloromethylphenylsilane is distilled (yield 16.4%)[17] or in the hydrolysis of $Cl(CH_3)C_6H_5Si(OC_6H_4C_6H_5\text{-}o)$[18]. $\alpha\omega$-Dichloro-oligodiphenylsiloxanes have been obtained by the hydrolysis of dichlorodiphenylsilane[19,20]. With a $(C_6H_5)_2SiCl_2 : H_2O$ molar ratio of 2 : 1, mainly 1,3-dichlorotetraphenyldisiloxane and 1,5-dichlorohexaphenyltrisiloxane are formed[19]. At the same time the formation of hexaphenylcyclotrisiloxane is observed. When the reactant ratio is reduced to 1.5, the yield of 1,3-dichlorotetraphenyldisiloxane falls and the yields of 1,5-dichlorohexaphenyltrisiloxane and hexaphenylcyclotrisiloxane increase. The theoretical yield of cyclosiloxane is reached when the $(C_6H_5)_2SiCl_2 : H_2O$ molar ratio is reduced to 1 − 0.67.

Hydrolysis of dichloromethylsilanes with an organic substituent, of the type $CH_3(RCH_2CH_2)SiCl_2$ (R = CF_3 or C_3F_7), in an autoclave by water saturated with hydrogen chloride (24 − 30°C, 28 − 48 h) yielded $\alpha\omega$-dichlorooligomethylsiloxanes with an organic substituent per unit, $Cl[CH_3(RCH_2CH_2)SiO]_nSiCH_3(RCH_2CH_2)Cl$, containing fluorine atoms in the organic group[21]. The oligomer $ClCH_3(CH_2Cl)SiO[CH_3(ClCH_2)SiO]_3SiCH_3(CH_2Cl)Cl$ was obtained similarly[22].

Hydrolysis of dichlorosilanes with two organic substituents can be carried out in the presence of salts of heterocyclic bases, acid amides, or triphenylphosphine. For example, when water is added to a mixture of dichlorodiphenylsilane and $C_5H_5N.HCl$ in toluene [molar ratio $(C_6H_5)_2SiCl_2 : H_2O = 2.5 : 1$] at 80 − 85°C, 1,3-dichlorotetraphenyldisiloxane is formed in 81.5 yield. The residue contains 1,5-dichlorohexaphenyltrisiloxane. $\alpha\omega$-Dichloro-oligomethyl- and $\alpha\omega$-dichloro-oligomethylphenyl-siloxanes were obtained similarly[23].

A conductimetric study of the hydrolysis of chlorosilane in a homogeneous medium (in a mixture of ethylene glycol with ether) showed that a decrease of reaction temperature and an increase of HCl content suppress the hydrolysis of Si − Cl bonds and promote the formation of the corresponding oligomers $Cl(R_2SiO)_nSiR_2Cl$.[24]

Linear $\alpha\omega$-difluoro-oligodiethylsiloxanes $F[(C_2H_5)_2SiO]_nSi(C_2H_5)_2F$ and also 8 − 10% of $(C_2H_5)_2SiF_2$ are formed in the hydrolysis of dichlorodiethylsilane with a saturated aqueous solution of potassium fluoride[25]. The study of the mechanism of the partial hydrolysis of dichlorosilanes with two organic substituents is of great importance for the determination of the optimum conditions in the preparation of $\alpha\omega$-dichloro-oligosiloxanes. This reaction is a complex process and the nature and proportions of the hydrolysis products depend on many factors ($R_2SiCl_2 : H_2O$ ratio, structure of R_2SiCl_2, solvent, reaction temperature, etc.). The formation of linear oligomers is promoted by an increase of the concentration of R_2SiCl_2, the homogeneity of the medium, and a low process temperature. It has been suggested[6,26] that partial hydrolysis is accompanied by a stepwise condensation:

$$Cl(R_2SiO)_nSiR_2Cl + H_2O \rightarrow Cl(R_2SiO)_nSiR_2OH,$$

$$2\,Cl(R_2SiO)_nSiR_2OH \rightarrow Cl(R_2SiO)_{2n+1}SiR_2Cl + H_2O \text{ etc.}$$

Evidence for this mechanism comes from the formation, during the hydrolysis of oligosiloxanes and polysiloxanes with two organic substituents per unit and mainly with a linear structure and from the high polydispersity of the oligomers and polymers obtained.

Low-molecular-weight $\alpha\omega$-dichlorosiloxanes are formed when t-butyl alcohol reacts with dichloromethylphenylsilane[15]. t-Butyl chloride, hydrogen chloride, polyisobutylene, and benzene are formed at the same time. The process is probably based on the hydrolysis of chlorosilanes by the water formed in the reaction of the liberated hydrogen chloride with t-butyl alcohol.

2. Telomerisation of Cyclosiloxanes with Halogenosilanes Having Organic Substituents

The telomerisation of cyclosiloxanes with halogenosilanes having organic substituents, which takes place according to the general mechanism

$$RR'SiCl_2 + n(R''R'''SiO)_x \rightarrow ClRR'Si(OSiR''R''')_{nx}Cl, \quad (x \geqslant 3)$$

was first achieved in 1960.[27-30] The reaction is carried out in sealed tubes (without a catalyst) at 250°C for 3 − 5 h. The difunctional oligomers $ClR(CH_3)Si(OSiR'R'')_{3n}Cl$ (R = R′ = R″ = CH_3; R = H, R′ = R″ = CH_3; R = CH_2=CH, R′ = R″ = CH_3; R = C_6H_5, R′ = R″ = CH_3; R = R′ = CH_3, R″ = C_6H_5; R = CH_3, R′ = R″ = C_6H_5) were obtained in this way from $R(CH_3)SiCl_2$ and $(R'R''SiO)_3$ [27,28,30-36]. The reactivities of halogenosilanes and cyclosiloxanes decrease in the series $CH_3SiHCl_2 > (CH_3)_2SiCl_2 > CH_3(CH_2=CH)SiCl_2 > CH_3(C_6H_5)SiCl_2$; $[(CH_3)_2SiO_3] > [(C_2H_5)_2SiO]_3 > [CH_3(C_6H_5)SiO]_3 > [CH_3(CH_2=CH)SiO]_3$. In all cases, instead of individual telomers, their mixtures are formed. A decrease of the molar ratio $RR'SiCl_2 : (R''R'''SiO)_3$ leads to a fall of the yield of low-molecular-weight telomers and a sharp increase of high-boiling telomerisation products.

With an equimolar ratio of dichlorodimethylsilane and hexamethylcyclotrisiloxane (D_3), telomers with $n = 1$ (64.4%), $n = 2$ (15.6%), $n = 3$ (4.1%), and $n \geqslant 4$ (10.9%) were obtained[31]. Telomers with $n = 1$ (83.1%), $n = 2$ (7.1%), $n = 3$ (3.1%), and $n \geqslant 4$ (3.9%) were obtained from dichloromethylsilane and D_3 (in proportions of 1 : 1); with a molar ratio of 1 : 2, the products were telomers with $n = 1$ (31.8%), $n = 2$ (42.8%), $n = 3$ (9.5%) and $n \geqslant 4$ (14.3%).[34] The reaction of dichloromethylvinylsilane with D_3 leads to the formation of a mixture of telomers with $n = 1$ (71.2%), $n = 2$ (11.8%), and $n \geqslant 3$ (8.7%). When the ratio is 1 : 2, the yields of telomers are 67.1% for $n = 2$ and 25.5% for $n \geqslant 3$. The telomer with $n = 1$ is not formed under these conditions[34].

Dichloromethylphenylsilane forms with D_3 (molar ratio 1:1) telomers with $n = 1$ (76.2%), $n = 2$ (77.6%), and $n \geq 3$ (13.6%).[34]

When 1,3,5-trimethyl-1,3,5-triphenylcyclotrisiloxane was cleaved by dichlorodimethylsilane, telomers with $n = 1$ (32.9%), $n = 2$ (4.9%), and $n \geq 3$ (63.9%), were obtained. The conversion of siloxane was 88.0% and that of dichlorodimethylsilane 36%.[35] The reaction in an autoclave is accompanied by the dissociation of siloxane bonds in the telomers.

Telomers could not be isolated from the products of the reaction of dichlorodimethylsilane with 1,3,5-trimethyl-1,3,5-trivinylcyclotrisiloxane because of the occurrence of a side process involving polymerisation with participation of the vinyl groups[35].

Hexaethylcyclotrisiloxane is cleaved by dichloromethylsilane with formation of oligomers in which $n = 1$ (64.3%), $n = 2$ (17.6%), and $n \geq 3$ (18.6%).[35] The reaction with dichlorodiethylsilane gives a 61.9% yield of 1,7-dichloro-octaethyltetrasiloxane[37].

1,7-Dichloro-1,3,5,7,7-pentaethyl-1,3,5-tri-n-propyltetrasiloxane (57%) and 1,7-dichloro-1,3,5,7-tetraethyl-1,3,5,7-tetra-n-propyltetrasiloxane (33%) were obtained by the cleavage of *sym*-triethyltri-n-propylcyclotrisiloxane with dichlorodiethylsilane and dichloroethyl-n-propylsilane respectively. 1,3,5,7-Tetra-n-butyl-1,7-dichloro-1,3,5,7-tetraethyltetrasiloxane was synthesised in 42% yield from *sym*-tetra-n-butyltetraethylcyclotrisiloxane and n-butyldichloroethylsilane[38].

D_4 enters into the telomerisation reaction with greater difficulty than D_3. Nevertheless oligomers of the type $ClR(CH_3)Si(OSiR'R'')_nCl$ ($R = R' = R'' = CH_3$; $R = C_6H_5$, $R' = R'' = CH_3$; $R = CH{=}CH_2$, $R' = R'' = CH_3$) have been obtained by the reaction of D_4 with $R(CH_3)SiCl_2$ ($R = CH_3$, C_6H_5, or $CH = CH_2$).[27,39].

When the ratio $D_4 : (CH_3)_2SiCl_2 = 2:1$, telomers with $n = 1$ (16.7%), $n = 2$ (20.0%), and $n = 3$ (7.7%) are formed and when the ratio is 1:1 the products have $n = 1$ (36.9%), $n = 2$ (33.0%), and $n = 3$ (7.5%). The reaction with a 3:1 reactant ratio was also investigated[33]. In all cases a mixture was obtained in which the telomer corresponding to the specified $D_4 : (CH_3)_2SiCl_2$ ratio predominated.

The reaction of equimolar amounts of dichloromethylvinylsilane and D_4 gave telomers with $n = 1$ (18.5%), $n = 2$ (30.8%), $n = 3$ (14.6%), and $n \geq 4$ (36.1%).[39] The reaction of dichloromethylphenylsilane with D_4 under standard conditions (250°C, 3 h) proceeds with the formation of small amounts of telomers (about 10 wt.%). Under more severe conditions (300°C, 5 h, molar ratio 2:1), the overall conversion reaches 18% and telomers with $n = 1$ (7.8%) and $n = 2$ (2.3%) are formed[39].

The synthesis of 1,9- dichlorodecamethylpentasiloxane (yield 34%) by heating a 1:1 mixture of dichlorotrimethylsilane and D_4 in an enamelled autoclave at 270–400°C and 80 atm has been described[40]. At 300°C the yield increases to 50%.

Changes in reactant ratio and temperature affect the yield of reaction products, which is a maximum for a ratio of 1:2–81% at 300°C and 77% at 350°C. At 400°C the yield falls to 42%. In all cases side products of the cleavage of the $-Cl[(CH_3)_2SiO]_nSi(CH_3)_2Cl$ chains with $n = 1$–6, 8, or 12 were obtained. When the reaction was carried out in an autoclave without a glass liner, a low yield of the required telomer was obtained together with a large amount of side products.

1,3-Dichlorotetramethyldisiloxane (22%), 1,5-dichlorohexamethyltrisiloxane (19%), 1,7-dichloro-octamethyltetrasiloxane (15%), higher oligomers (26%), and also D_3 (0.2%) and D_4 (1.0%) were obtained by heating polydimethylsiloxane with dichlorodimethylsilane in a bomb (380–400°C 5 h). In the presence of a catalyst ($FeCl_3$ and HCl or HBr), the reaction takes place also at room temperature[41].

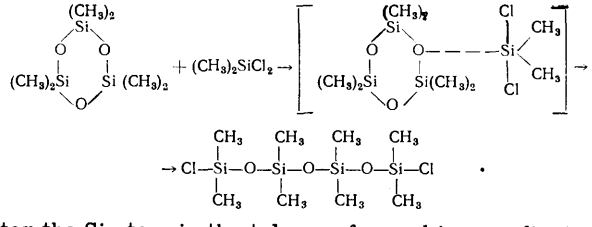
Oligomers containing together with Si–Cl bonds functional groups in the organic substituents were obtained by the reaction of D_3 with alkyl(chloroalkyl)chlorosilanes containing chlorine atoms in the α-, β-, and γ-positions[42] and by the reaction of D_4 with dichloro-(3,3,3-trifluoropropyl)methylsilane[42].

The position of the halogen atom in the hydrocarbon group of dichloro(halogenoalkyl)methylsilanes has a significant influence on the telomerisation reaction[42]. Thus dichloro(chloromethyl)methylsilane reacts with D_3 to form not only the telomers $Cl[(CH_3)_2SiO]_{3n}.SiCH_3(CH_2Cl)Cl$ with $n = 1$ (43.7%) and $n = 2$ and 3 but also their dissociation products containing 2, 3, and 4 silicon atoms in the molecule in yields of 18.3, 16.5, and 12.5% respectively. Dichloro-(2-chloroethyl)methylsilane reacts with D_3 to form telomers in which $n = 1$ (39.1%) and $n = 2$ (10.5%) and dissociation side products. The reaction of dichloro-(3-chloropropyl)methylsilane with D_3 is strictly of the telomerisation type with formation of telomers in which $n = 1$ (63.0%) and $n = 2$ (4.8%). The reactivity of dichloro(chloroalkyl)methylsilanes in the reaction with D_3 falls in the sequence $\beta > \alpha > \gamma$ as the position of the chlorine atom in the alkyl group is varied.

The reaction of D_4 with dichloro-(3,3,3-trifluoropropyl)methylsilane at 250°C involves the formation of a mixture of $Cl[(CH_3)_2SiO]_{4n}SiCH_3.(CF_3CH_2CH_2)Cl$ telomers with $n = 1$ (28.4%), $n = 2$ (7%), and $n = 3$ (10%) for the equimolar reactant ratio and with $n = 1$ (16.2%), $n = 2$ (22%), and $n = 3$ (20%) for the 2:1 ratio. The reaction proceeds mainly as in the case of dialkyldichlorosilanes. The polar and steric effects of the 3,3,3-trifluoropropyl group influence only the yield of the telomers. It proved possible to obtain 1,7-dichloro-octamethyltetrasiloxane and 1,9-dichlorodecamethylpentasiloxane by the cleavage of D_4 with dichlorodimethylsilane (molar ratio 1:4–4:1) in the presence of an equimolar amount of dimethylformamide, its derivatives, or *N*-formylpiperidine at 20°C in 120 h.[44]

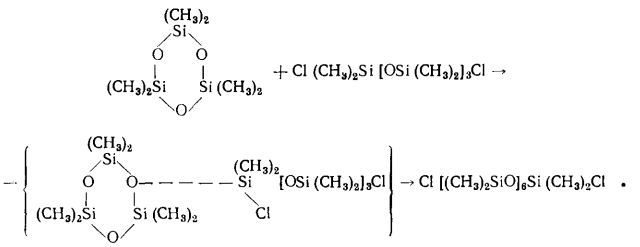
In the presence of a catalyst ($FeCl_3$) the telomerisation reaction is complicated by a side reaction involving the cleavage of telomer ins[36]. The reaction of D_3 with $(CH_3)_2SiCl_2$ results in the formation of the oligomers $Cl[(CH_3)_2SiO]_mSi(CH_3)_2Cl$ in which the number of silicon atoms *m* ranges from 2 to 7. In the presence of $FeCl_3$ linear siloxanes can also enter into the telomerisation reaction with dialkyldihalogenosilanes[45].

The study of the mechanism of the telomerisation reaction[27,32] led to the hypothesis that an intermediate complex of the cyclosiloxane and halogenosilane is formed in the first reaction stage and is subsequently converted into the first member of the homologous series:

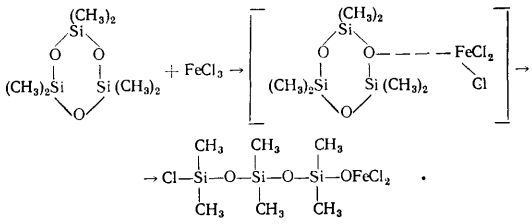


Later the Si atom in the telomer formed is coordinated to the oxygen atom of a new cyclosiloxane molecule as a

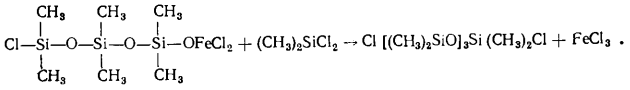
result of which the next member of the homologous series is formed, etc.



In the presence of a catalyst ($FeCl_3$) the reaction becomes reversible[32]. Together with telomers, dissociation products containing 1, 2, 3, and more silicon atoms in the molecule are formed. In this case a molecule of iron(III) chloride is coordinated to the oxygen atom of the cyclosiloxane of the telomer and the resulting complex decomposes via the mechanism



The Si–OFe bond is unstable and under the influence of compounds containing the Si–Cl bond breaks down with liberation of $FeCl_3$ and the formation of the Si–O–Si bond:



3. Cleavage of Cyclosiloxanes by Organic and Inorganic Halogen-containing Compounds

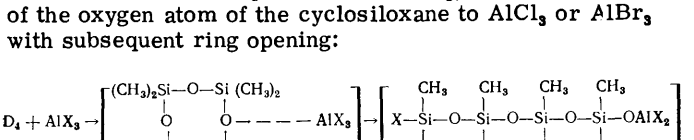
$\alpha\omega$-Dihalogeno-oligodialkylsiloxanes are formed when cyclosiloxanes or linear siloxanes are heated with boron, aluminium, phosphorus, or antimony halides:

$$(RR'SiO)_n + MX_n \rightarrow X(RR'SiO)_mSiRR'X \quad (M=B, Al, P, Sb) .$$

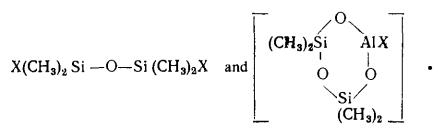
For example, oligomers of the $Cl(RR'SiO)_nSiRR'Cl$ series, where $R = R' = CH_3$,[46] $R = R' = C_2H_5$,[46,47] or $R = CH_3$ and $R' = C_6H_5$,[47] were obtained by the cleavage of the corresponding cyclotrisiloxanes and cyclotetrasiloxanes with aluminium chloride.

Difficult to obtain $\alpha\omega$-dibromo-oligosiloxanes, for example 1,3-dibromotetramethyldisiloxane, 1,5-dibromohexamethyltrisiloxane, and 1,7-dibromo-octamethyltetrasiloxane, have been synthesised by the reaction of D_4 with $AlBr_3$.[48] 1,3-Difluoro- and 1,3-dichlorotetramethyldisiloxanes are formed when cyclosiloxanes are cleaved with BF_3 or BCl_3 respectively[49,50].

It is suggested[48] that the first stage of the reaction of cyclosiloxanes with $AlCl_3$ and $AlBr_3$ is, as in the telomerisation in the presence of $FeCl_3$, the coordination of the oxygen atom of the cyclosiloxane to $AlCl_3$ or $AlBr_3$ with subsequent ring opening:

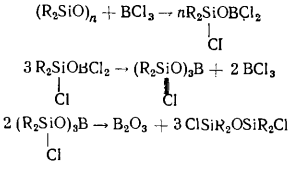


The linear aluminosiloxane formed decomposes into



Under the influence of AlX_3, 1,3-dihalogenotetramethyldisiloxane rearranges to higher $\alpha\omega$-dihalogenopolysiloxanes[48].

It has been suggested[50] that the dialkylchlorosiloxyborates formed initially in the reaction with BCl_3 decompose into the corresponding chlorosiloxanes and B_2O_3:



$\alpha\omega$-Dichloro-oligosiloxanes are also obtained by the distillation of cyclic or linear polysiloxanes with phosphorus oxide halides, antimony halides, or the halides of aromatic acids (benzoyl, phthaloyl, or isophthaloyl chlorides) in the presence of $FeCl_3$.[51]

$\alpha\omega$-Dichloro-oligoalkylmethylsiloxanes, in which the alkyl group contains three and more fluorine atoms, have been obtained by the cleavage with hydrochloric acid (at 30°C and an elevated pressure) of the hydrolysis product of $CH_3(RCH_2CH_2)SiCl_2$ ($R = CF_3$ or C_3F_7).[21]

4. Heterofunctional Condensation Reactions

The heterofunctional condensation reaction, which proceeds according to the general mechanism $\equiv Si-X + RO-Si\equiv \rightarrow \equiv Si-O-Si\equiv$ where X = halogen and R = H, alkyl, or acyl, has been less frequently used to synthesise $\alpha\omega$-difunctional oligomers than the hydrolysis of chlorosilanes with organic substituents and the cleavage of cyclosiloxanes. An advantage of this method over those described above is the possibility of obtaining oligomers with a specified alternation of different substituents at the Si atoms.

When dichloromethylsilane, dichlorodimethylsilane, dichloroethylsilane and dichlorodiethylsilane are heated with chloroethoxydimethylsilane (60–80°C, $FeCl_3$ catalyst), the corresponding $\alpha\omega$-dichloro-oligodialkylsiloxanes containing both identical and mixed alkyl substituents are formed[52]:

$$R_2SiCl_2 + R_2SiCl(OR) \rightarrow Cl(SiR_2O)SiR_2Cl + n\,HCl .$$

The reaction proceeds according to the mechanism

$$ClSiR_2-Cl + C_2H_5O-SiR_2'-Cl \rightarrow ClSiR_2-O-SiR_2'Cl + C_2H_5Cl ,$$

$$ClSiR_2OSiR_2'Cl + C_2H_5O-SiR_2'-Cl \rightarrow ClSiR_2-OSiR_2'-O-SiR_2'Cl + C_2H_5Cl, \text{ etc.}$$

The oligomers $Cl[(CH_3)_2SiO]_nSi(CH_3)_2Cl$ with $n = 1-3$ have been obtained by this method from dichlorodimethylsilane and chloroethoxydimethylsilane (1 : 1 molar ratio) in proportions analogous to those obtained in the partial hydrolysis of dichlorodimethylsilane [$n = 1$ (28%), $n = 2$ (24%), $n = 3$ (15%), and $n = 5$ and 6 (2%)][9,10]; 22% of the initial $(CH_3)_2SiCl_2$ does not react, whereas $(CH_3)_2Si(OC_2H_5)Cl$ reacts completely. The formation of cyclosiloxanes was not observed.

The reaction of dichlorodiethylsilane with chloroethoxydimethylsilane (1 : 1) leads to the corresponding $\alpha\omega$-dichloro-oligodialkylsiloxanes containing preferentially 4 and 5 silicon atoms in the molecule.

When the concentration of $(C_2H_5)_2SiCl_2$ is increased (up to a molar ratio of 2 : 1), the yield of low-molecular-weight $\alpha\omega$-dichloro-oligosiloxanes $Cl[(CH_3)_2SiO]_nSi(C_2H_5)_2Cl$, containing between 2 and 5 silicon atoms [$n = 1$ (14%), $n = 2$ (13.7%), and $n = 3$ (5%)], increases. In the case of dichloromethylsilane and dichloroethylsilane, the main heterofunctional condensation reaction is accompanied by disproportionation [52]:

$$CH_3SiHCl_2 + (CH_3)_2Si(OC_2H_5)Cl \rightarrow CH_3SiH(OC_2H_5)Cl + (CH_3)_2SiCl_2 .$$

The extremely reactive chloroethoxymethylsilane readily reacts with alkyldichlorosilanes [52]:

$$CH_3HSi(OC_2H_5)Cl + CH_3SiHCl_2 \rightarrow Cl(CH_3)SiHOHSi(CH_3)Cl + C_2H_5Cl .$$

Apart from the main products of the heterofunctional condensation of dichloromethylsilane and dichloroethylsilane with chloroethoxydimethylsilane

$Cl[(CH_3)HSiO]_nSi(CH_3)_2Cl$ [$n = 1$ (10%) and $n = 2$ (2.2%)] and $Cl[(C_2H_5)HSiO]_nSi(CH_3)_2Cl$ [$n = 1$ (7.7%) and $n = 2$ (8.8%)], the products $Cl[(CH_3)HSiO]_nSi(CH_3)HCl$ [$n = 1$ (18.3%) and $n = 2$ (6.2%)] and $Cl[(C_2H_5)HSiO]_nSi(C_2H_5)HCl$ [$n = 1$ (8.1%) and $n = 2$ (3.3%)] were also isolated.

Heterofunctional condensation of silanediols containing two organic substituents with dichlorosilanes (1 : 2), also containing two organic substituents, in the presence of aniline yielded the corresponding hexa-alkyl-1,5-dichlorotrisiloxanes [53]:

$$2\,RR'SiCl_2 + R''R'''Si(OH)_2 \rightarrow ClSiRR'OSiR''R'''OSiRR'Cl + 2\,HCl$$

($R = R' = CH_3$, $R'' = C_6H_5$, $R''' = CH_3$; $R = R' = C_6H_5$, $R'' = R''' = CH_3$; $R = R' = C_6H_5$, $R'' = C_6H_5$, $R''' = CH{=}CH_2$; $R = R' = C_6H_5$, $R'' = CH_3$, $R''' = C_2H_5$; $R = R' = C_6H_5$, $R'' = CH_3$, $R''' = CH_2CH(CH_3)C_6H_5$; $R = R' = C_6H_5$, $R'' = CH_3$, $R''' = CH_2CH_2CF_3$).

1,5-Dichloro-1,1,5,5-tetramethyl-3,3-diphenyltrisiloxane is formed in 66% yield on condensation of diphenylsilanediol with dichlorodimethylsilane (1 : 2) in the presence of a solvent and a hydrogen chloride acceptor (pyridine) [54].

5. Other Reactions

Dialkyldihalogenosilanes can react with metal oxides whereby they are converted into $\alpha\omega$-dihalogenosiloxanes. Metal oxides serve as a source of oxygen necessary for the formation of the Si–O–Si bond. Dichlorodimethylsilane reacts with Fe_2O_3 to form 1,3-dichlorotetramethyldisiloxane [55]. However, according to other data [56], anhydrous Fe_2O_3 does not react with $(CH_3)_2SiCl_2$ to form the above compound and therefore its synthesis requires the addition of a small amount of water. Instead of water, one can introduce at the beginning of the reaction a small amount of hydrogen chloride. Evidently chlorodimethylsilanol is formed in the first stage as a result of the hydrolysis of $(CH_3)_2SiCl_2$. Subsequently Fe_2O_3 apparently behaves as an acceptor of hydrogen chloride and a donor of water promoting the heterofunctional condensational reaction:

$$R_2SiCl_2 + H_2O \rightarrow R_2Si(Cl)OH + HCl ,$$
$$3\,R_2Si(Cl)OH + 3\,R_2SiCl_2 + 0.5\,Fe_2O_3 \rightarrow 3\,ClR_2SiOSiR_2Cl + FeCl_3 + 1.5\,H_2O .$$

The reaction of chlorodimethylsilanol with $(CH_3)_2SiCl_2$, which leads to the formation of oligomers, takes place according to the mechanism

$$Cl(CH_3)_2SiOH + (CH_3)_2SiCl_2 \xrightarrow{Fe_2O_3} Cl(CH_3)_2SiOSi(CH_3)_2Cl + HCl ,$$
$$Cl(CH_3)_2SiOH + Cl(CH_3)_2SiOSi(CH_3)_2Cl \rightarrow Cl(CH_3)_2SiOSi(CH_3)_2OSi(CH_3)_2Cl + HCl \text{ etc.}$$

PbO, CaO, MgO, ZnO, CuO, [57,58] BeO, and Ag_2O [58] have also been used as oxygen donors.

Dichlorodimethylsilane reacts with ethanol in the presence of catalytic amounts of $FeCl_3$, forming 1,2-dichlorotetramethyldisiloxane [up to 69% of $(CH_3)_2SiCl_2$ which has reacted] and 1,5-dichlorohexamethyltrisiloxane (21%). [59]

The mechanism of the catalytic effect of iron(III) chloride probably consists of the following steps:

$$3\,C_2H_5OH + FeCl_3 \rightarrow 3\,C_2H_5Cl + Fe(OH)_3 ,$$
$$3\,Fe(OH)_3 + 3\,HCl \rightarrow FeCl_3 + 3H_2O .$$

An interesting method for the preparation of chloro-oligomers is based on the chlorination of hydrosiloxanes containing linkages between H and Si atoms [60,61], for example:

$$H[(CH_3)_3SiO]_2SiO\{SiO[OSi(CH_3)_3]_2\}_nSi[OSi[OSi(CH_3)_3]_2H \quad (n \geqslant 0)$$

or

$$HR(CH_3)Si\{OSi[OSi(CH_3)_3]_2\}_nOSi(CH_3)RH \quad (R = CH_3, C_6H_5 \text{ и } n \geqslant 1) .$$

III. METHODS OF SYNTHESIS OF $\alpha\omega$-DIACYLOXY-OLIGOSILOXANES

1. The Cleavage of Cyclosiloxanes by Carboxylic Acid Anhydrides and Diacetoxydimethylsilane

$\alpha\omega$-Diacyloxyoligosiloxanes have been little investigated compared with other organosilicon oligomers. At the same time $\alpha\omega$-diacyloxysiloxanes containing reactive acyloxy-groups at the end of the chain are very promising and interesting oligomers from which it is possible to obtain a large number of a wide variety of organosilicon compounds.

The most important method of synthesising $\alpha\omega$-diacyloxyoligosiloxanes containing two organic substituents per unit consists in the cleavage of cyclosiloxanes by carboxylic acid anhydrides.

Acetic anhydride cleaves cyclosiloxanes containing two organic substituents (preferably in the presence of catalysts), forming $\alpha\omega$-diacetoxyoligosiloxanes with two organic substituents per unit:

$$(R_2SiO)_n + (CH_3CO)_2O \rightarrow CH_3COO(R_2SiO)_nCOCH_3 .$$

For example, $\alpha\omega$-diacetoxyoligodimethylsiloxanes $CH_3COO[(CH_3)_2SiO]_n.COCH_3$ ($n = 2$ or 3) are formed on catalytic cleavage of D_4 by acetic anhydride (molar ratio about 1 : 5) in the presence of sulfuric acid [62]. A deficiency of this method is the low conversion of D_4 (about 60%), the long duration of the reaction (40 h), and the high yield of diacetoxydimethylsilane, which constitutes about one third of all the reaction products. This reaction is of little interest for the synthesis of diacetoxydimethylsilane, since the latter can be readily obtained directly from dichlorodimethylsilane and acetic anhydride (see, for example, Dolgov et al. [63]).

The use of anhydrous iron(III) chloride or zinc chloride [64–66] as catalysts permits an increase of the conversion of D_4 to 95% and a reduction of the reaction time

to 1.5–4 h. Then oligomers with four and five silicon atoms in the molecule appear in the mixture and the overall yield of oligomers increases [$n = 2$ (20%), $n = 3$ (14%), $n = 4$ (11%), and $n = 5$ (6%); the yields are given relative to the initial reactants]. Diacetoxydimethylsilane is formed in yields up to 5%.

The reaction of D_4 with acetic anhydride involving the formation of $\alpha\omega$-diacetoxyoligodimethylsiloxanes can take place also in the absence of catalysts, provided that it is carried out at 250–260°C under pressure (in an autoclave or a sealed glass tube)[67]. The composition of the oligomers obtained in the autoclave is approximately the same as in the cleavage of D_4 by acetic anhydride in the presence of $FeCl_3$. In the reaction in a sealed glass tube the amount of oligomer with $n = 2$ is lower and that of the oligomer with $n = 5$ somewhat higher [$n = 2$ (14.3%), $n = 3$ (10%), $n = 4$ (9.8%), and $n = 5$ (9.6%)].

$\alpha\omega$-Diacetoxyoligosiloxanes with two organic substituents per unit, containing 3,3,3-trifluoropropyl, ethyl, vinyl, and phenyl groups at the silicon atoms, were obtained similarly from the corresponding cyclosiloxanes $(RR'SiO)_m$ and acetic anhydride[68,69]. The yields of the oligomers are given in Table 1. The conversion of octaethylcyclotetrasiloxane and 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane is 85–90%. 1,3,5-Trimethyl-1,3,5-triphenylcyclotrisiloxane cannot be isolated from the reaction mixture, since the reaction products begin to decompose on distillation under the influence of the high temperature and the $FeCl_3$ present even before the distillation of the cyclosiloxane begins.

Table 1. Composition of mixtures of $\alpha\omega$-diacetoxysiloxanes with two organic substituents $[CH_3COO(RR'SiO)_nCOCH_3]$ formed when $(RR'SiO)_m$ is cleaved with acetic anhydride[69].

$CH_3COO(RR'SiO)_nCOCH_3$	R=CH₃; R'=CF₃CH₂CH₂		R=CH₃ R'=CH₂=CH	R=R'=C₆H₅	R=CH₃ R'=C₆H₅
	m=3	m=4*	m=4	m=3+4	m=3
n=2	17.7	8.3	11.4	30.3	14.8
n=3	23.0	36.1	12.1	19.7	8.1
n=4	15.2	9.7	10.9	10.9	—
n=5	—	—	2.8	—	—

* The reaction was carried out in an autoclave in the absence of $FeCl_3$.

1,3,5-Tri-(3,3,3-trifluoropropyl)-1,3,5-trimethylcyclotrisiloxane is completely cleaved by acetic anhydride, while 1,3,5,7-tetra-(3,3,3-trifluoropropyl)-1,3,5,7-tetramethylcyclotetrasiloxane is cleaved only to the extent of 30%. When the reaction is carried out in an autoclave (without a catalyst) at 250–260°C, the tetrasiloxane is cleaved almost completely.

When $HClO_4$ is employed as a catalyst, the temperature of the reaction in which cyclosiloxanes are cleaved by acetic anhydride may be reduced[70]. For example, when acetic anhydride is allowed to react with hexaethylcyclotrisiloxane (molar ratio 1 : 1) in the presence of perchloric acid, 1,3-diacetoxyhexaethyltrisiloxane is formed in a yield up to 30% even at room temperature. 1,3-Diacyloxytrisiloxanes with six organic substituents, $R'COO[C_2H_5(R)SiO]_3COR'$, were obtained by the cleavage of the corresponding cyclosiloxanes by carboxylic acid anhydrides in the presence of $ZnCl_2$ at 100°C or without a catalyst at 250°C (in a sealed tube)[70]. The yields of the oligomers are given in Table 2.

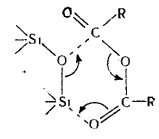
Boron triacetate has also been used as a catalyst of the cleavage of polysiloxanes by carboxylic acid anhydrides[71].

Oligodimethylsiloxanes blocked by perfluoroacyloxy-groups have been obtained by the cleavage of D_4 with perfluorocarboxylic acid anhydrides (in a sealed glass tube)[72]. With a D_4 : heptafluorobutyric acid anhydride molar ratio of 1 : 1, the cleavage products are the oligomers $CF_3CF_2CF_2COO[(CH_3)_2SiO]_nCOCF_2CF_2CF_3$ with $n = 2$ (27%) and $n = 4$ (30%) and also a mixture of oligomers with $n = 5$ and 6. When the ratio of the initial reactants is increased to 9 : 1, a viscous liquid polymer with $\bar{M} = 3840$ is formed. A similar polymer was obtained also in the reaction of D_4 with trifluoroacetic acid anhydride (molar ratio 10 : 1). When D_4 was cleaved with butyric anhydride, a mixture of oligomers with $n = 2$ (25.8%), $n = 3$ (14.8%), and $n \simeq 7$ (57%) was obtained.

Table 2. The yield of $R'COO[C_2H_5(R)SiO]_3COR'$ obtained by the cleavage of $[C_2H_5(R)_3SiO]_3$ with $(R'CO)_2O$.[70]

R	R'	Yield of trisiloxane, %		R	R'	Yield of trisiloxane, %	
		in sealed tube 250°C	in the presence of $ZnCl_2$ at 100°C			in sealed tube 250°C	in the presence of $ZnCl_2$ at 100°C
C_2H_5	CH_3	33.0	63.5	C_2H_5	C_2H_5	22.4	44.8
CH_3	CH_3	—	28.1	C_2H_5	C_4H_9	29.2	41.0
C_3H_7	CH_3	16.8	42.0	C_2H_5	C_6H_{11}	20.7	46.8

The cleavage of cyclosiloxanes by carboxylic acid anhydrides is probably reversible. The composition of the products of the reaction of D_4 with acetic anhydride is independent of the nature of the initial cyclosiloxane (D_3, D_4, D_5, "depolymerisation mixture", and a mixture of cyclic and linear siloxanes) and is determined only by the ratio of the initial reactants[66]. It has been suggested[73] that the cleavage of siloxanes proceeds via the intermediate formation of a six-membered cyclic activated complex involving the Si–O bond and the reactant. As a result of the delocalisation of six electrons in the ring formed, the energy required for the activation of the molecule diminishes, which facilitates cleavage. Similarly, in the cleavage of cyclosiloxanes by acid anhydrides, an intermediate cyclic complex is formed in the first reaction stage (with or without the participation of the catalyst):



which on decomposition gives rise to an $\alpha\omega$-diacyloxysiloxane oligomer with the same number of silicon atoms as in the initial ring:

$$(R_2SiO)_n + (R'CO)_2O \rightarrow R'COO(R_2SiO)_nCOR' .$$

The formation of homologues of this oligomer with a greater or smaller number of silicon atoms in the linear chain takes place via the following reactions.

1. Homofunctional condensation via the acyloxy-groups:

$$2\,R'COO(R_2SiO)_nCOR' \rightarrow R'COO(R_2SiO)_{2n}COR' + (R'CO)_2O .$$

2. Cleavage of the cyclosiloxane by a diacyloxysilane or a diacyloxysiloxane:

$$(R_2SiO)_n + R'COO(R_2SiO)_mCOR' \rightarrow R'COO(R_2SiO)_{n+m}OCOR'.$$

3. Cleavage of the $\alpha\omega$-diacyloxysiloxane by a carboxylic acid anhydride:

$$R'COO(R_2SiO)_nCOR' + (R'CO)_2O \rightarrow R'COO(R_2SiO)_mCOR' + R'COO(R_2SiO)_{n-m}COR'.$$

4. Redistribution of the chains (mutual cleavage) of two molecules of $\alpha\omega$-diacyloxysiloxanes:

$$R'COO(R_2SiO)_nCOR' + R'COO(R_2SiO)_mCOR' \rightarrow R'COO(R_2SiO)_kCOR' + RCOO(R_2SiO)_pCOR'.$$

The possibility of such reactions has been confirmed as follows. When diacetoxymethylphenylsilane is heated at 200–260°C, acetic anhydride and cyclic polymethylphenylsiloxanes are formed[74]. Heating of individual $\alpha\omega$-diacetoxydimethylsiloxanes containing between two and five silicon in the molecule and of diacetoxydimethylsilane, both in the presence of a catalyst and without it, leads to the formation of $\alpha\omega$-diacetoxyoligodimethylsiloxanes both with a smaller and a greater number of silicon atoms compared with the initial oligomer[75,76]. The reaction mixture contains acetic anhydride and a small amount of cyclosiloxanes.

$\alpha\omega$-Diacyloxysiloxanes with two organic substituents are formed from cyclosiloxanes (D_3 and D_4) and acyloxysilanes or acyloxysiloxanes in the presence of catalysts (aprotic Lewis acids)[77]. Thus the reaction of D_3 with diacetoxydimethylsilane in the presence of $ZnCl_2$ yielded 1,7-diacetoxyoctamethyltetrasiloxane and 1,13-diacetoxytetradecamethylheptasiloxane. In the absence of a catalyst, high-molecular-weight polysiloxanes are formed.

2. Cleavage of Cyclosiloxanes by Carboxylic Acid Halides

$\alpha\omega$-Diacetoxyoligodimethylsiloxanes are the main products of the cleavage of D_4 by acetyl halides (acetyl chloride and fluoride)[78,79]. The reaction proceeds both in the presence of a catalyst ($FeCl_3$) and without it (in an autoclave). At the same time the corresponding dihalogenodimethylsilane and 1,3-dihalogenotetramethyldisiloxane are formed:

$$(R_2SiO)_4 + CH_3COX \rightarrow CH_3COO(R_2SiO)_nCOCH_3 + X(R_2SiO)_mSiR_2X,$$

where R = CH_3, X = Cl or F, n = 1–5, and m = 0 or 1.

3. Exchange Reactions of the Terminal Groups and Heterofunctional Condensation

These reactions are less important for the preparation of $\alpha\omega$-diacyloxyoligosiloxanes than those described previously, since they require a preliminary synthesis of oligosiloxanes containing other functional groups at the end of the chain. Nevertheless exchange reactions are employed for the synthesis of specific individual oligomers in high yields.

Reactions involving the substitution of Cl atoms by acyloxy-groups in the corresponding $\alpha\omega$-dichloro-oligosiloxanes by treating the latter with carboxylic acid anhydrides[80–82] or carboxylic acid salts[83,84] are most often used. Thus 1,3-diacetoxytetramethyldisiloxane and 1,5-diacetoxyhexamethyltrisiloxane are formed in yields of 60–75%[80] and 82–86%[81] on heating 1,3-dichlorotetramethyldisiloxane or 1,5-dichlorohexamethyltrisiloxane with acetic anhydride (in proportions of 1 : 2), with simultaneous distillation of the acetyl chloride formed:

$$Cl[(CH_3)_2SiO]_nSi(CH_3)_2Cl + 2(CH_3CO)_2O \rightarrow$$
$$\rightarrow CH_3COO[(CH_3)_2SiO]_nSi(CH_3)_2COCH_3 + 2CH_3COCl.$$

1,7-Diacetoxyoctamethyltetrasiloxane and 1,9-diacetoxydecamethylpentasiloxane were obtained similarly in 86% yield[81].

The products of the reaction of the corresponding $\alpha\omega$-dichloromethylphenylsiloxanes with acetic anhydride are $\alpha\omega$-diacetoxyoligomethylphenylsiloxanes[82]. $\alpha\omega$-Diacetoxydimethylsiloxanes containing at the ends of the chain acryloyloxy- or methacryloyloxy-groups are formed in yields up to 90% when an $\alpha\omega$-dichloro-oligosiloxane containing a sulphate group, $Cl[(CH_3)_2SiO]_{7.4}[(CH_3)_2SiOSO_2O]_{0.17}SiR_2Cl$, reacts with potassium methacrylate or acrylic acid[84].

The reaction of oligosiloxane-$\alpha\omega$-diols with carboxylic acids, their anhydrides, and chlorides has been described[83]:

$$HO(R_2SiO)H + 2R'COX \rightarrow R'COO(R_2SiO)_nCOR' + HX \quad (X=OH,Cl,OCOR').$$

Heterofunctional condensation of dialkyl(aryl)silanediols with dialkyl(aryl)diacetoxysilanes in the presence of a solvent and an acetic acid acceptor (pyridine) makes it possible to obtain diacetoxytrisiloxanes $RR'Si[OSi(R''R''')OCOCH_3]_2$ [53] (R = R' = C_6H_5, R'' = C_6H_5, R''' = CH_3 or R'' = R''' = CH_3; R = CH_3, R' = $CH{=}CH_2$, R'' = R''' = CH_3; R = C_6H_5, R' = CH_3, R'' = R''' = C_6H_5) in yields up to 90%.

High-molecular-weight $\alpha\omega$-diacetoxypolysiloxanes are formed when poly(siloxane-$\alpha\omega$-diols) are condensed with acetic anhydride or with a diacetoxysilane (diacetoxysiloxane) containing two organic substituents in the presence of nitrogenous bases[85].

4. Homofunctional Condensation

On heating, diacetoxydimethylsilane can condense with the formation of $\alpha\omega$-diacetoxyoligosiloxanes[75,76]. Thus, when $(CH_3)_2Si(OCOCH_3)_2$ was heated with $FeCl_3$ at 150°C, diacetoxyoligosiloxanes with n = 2 (27.7%), n = 3 (11.5%), and n = 4 (5%) were obtained.

Since diacetoxydimethylsilane is readily formed from dichlorodimethylsilane, there is a possibility of synthesising oligomers directly from dichlorodimethylsilane. The latter is heated with acetic anhydride until the evolution of the theoretical amount of acetyl chloride, then $FeCl_3$ is added, and, after heating, $\alpha\omega$-diacetoxyoligodimethylsiloxanes are distilled off[75]:

$$(CH_3)_2SiCl_2 + (CH_3CO)_2O \xrightarrow{-CH_3COCl} (CH_3)_2Si(OCOCH_3)_2 \xrightarrow{FeCl_3} \rightarrow$$
$$\rightarrow CH_3COO[(CH_3)_2SiO]_nCOCH_3 + (CH_3CO)_2O.$$

The homofunctional condensation of $\alpha\omega$-diacyloxyoligosiloxanes was mentioned in section III, 1.

IV. METHODS OF SYNTHESIS OF $\alpha\omega$-DIALKOXYOLIGOSILOXANES

1. Cleavage of Cyclosiloxanes by Alcohols and Alkoxysilanes

$\alpha\omega$-Dialkoxyoligosiloxanes with two organic substituents can be obtained directly from cyclosiloxanes by their catalytic cleavage with alcohols: $(R_2SiO)_n + 2R'OH \rightarrow R'O(R_2SiO)_nR' + H_2O$; acids[86–88], alkalis[86], or amines[89,90]

may be employed as catalysts for this reaction. For example, hexamethyl-1,5-di-n-octyloxytrisiloxane and hexaethyl-1,5-di-n-octyloxytrisiloxane were obtained by the cleavage of the corresponding cyclotrisiloxanes and cyclotetrasiloxanes (containing organic substituents) by n-octyl alcohol in the presence of an acid (toluene-*p*-sulphonic acid) or an alkaline (sodium methoxide) catalyst with simultaneous distillation of the water formed[86]. The best yield is achieved when the reaction is stopped after distilling off only 33% of the theoretical amount of water formed in the reaction and removing the catalyst.

When 1,3,5-trimethyl-1,3,5-triphenylcyclotrisiloxane is heated with alcohols in the presence of hydrochloric acid or KIL activated clay, 1,5-dialkoxymethylphenylsiloxanes $RO[CH_3(C_6H_5)SiO]_3R$ ($R = C_2H_5$, n-C_3H_7, or iso-C_3H_7) are formed in yields up to 72–86%[87]. Hydrochloric acid, perchloric acid, or an aluminosilicate may be employed as catalysts[88]. The reaction is significantly influenced by the size of the cyclosiloxane ring, the nature of the substituents at the silicon atoms, and the catalyst. Hexa-alkylcyclotrisiloxanes containing a strained six-membered ring are cleaved more readily than the unstrained octa-alkylcyclotetrasiloxanes.

When $[CH_3(C_6H_5)SiO]_3$ is cleaved with alcohols, individual alkoxy-derivatives are formed, whereas the cleavage of $[CH_3(C_6H_5)SiO]_4$ gives a polydisperse mixture. This is because the rate of cleavage of 1,3,5,7-tetramethyl-1,3,5,7-tetraphenylcyclotetrasiloxane is comparable to the rates of the secondary processes (reactions of the alcohol with the alkoxysiloxanes)[87]. However, the effect of ring size is somewhat reduced when sodium methoxide is employed as a catalyst[86].

In the presence of an acid catalyst, cyclosiloxanes can be arranged in the following sequence in terms of their decreasing reactivity with respect to alcohols: $D_3 > D_4 >$ hexaethylcyclotrisiloxane > octaethylcyclotetrasiloxane > octaphenylcyclotetrasiloxane. In the presence of an alkoxide, the order of the reactivities of cyclosiloxanes alters somewhat: $D_3 = D_4 >$ hexaethylcyclotrisiloxane > octaphenylcyclotetrasiloxane > octaethylcyclotetrasiloxane, i.e. the rate of cleavage of octaphenylcyclotetrasiloxane becomes higher than that of octaethylcyclotetrasiloxane. The explanation is that in acid cleavage the inductive and steric effects of phenyl groups reduce the reactivity of the siloxane bond in relation to the electrophilic agent by decreasing the electron density at the oxygen atom and screening the Si–O bond (by the phenyl groups).

In alkaline cleavage the inductive effect of phenyl groups promotes a nucleophilic attack on the Si atom, while the inductive and steric effects of ethyl groups hinder it[86].

When an excess of alcohol is used, cyclosiloxanes are completely cleaved to the corresponding dialkoxysilanes with two other organic substituents[90]:

$$1/n\,(R_2SiO)_n + 2R'OH \xrightarrow{R'O^-} R_2Si(OR')_2 + H_2O\ .$$

1,3-Dibutoxytetramethyldisiloxane is formed in a yield of up to 40% when D_4 is heated with tetrabutyl orthotitanate at 200°C for 4 h. Dibutoxydimethylsilane and a polymer are formed at the same time[91].

$\alpha\omega$-Alkoxyoligosiloxanes can be obtained also by the reaction of cyclic or linear polydimethylsiloxanes with alkoxysilanes[92]. For example the reaction of a linear polydimethylsiloxane with tri-n-butoxymethylsilane catalysed by KOH yielded tetra-n-butoxy-1,3-dimethyldisiloxane and penta-n-butoxy-1,3,5-trimethyltrisiloxane:

$$[-Si(CH_3)_2OSi(CH_3)_2]_n + CH_3Si(OC_4H_9\text{-}n)_3 \rightarrow (n\text{-}C_4H_9O)_2Si(CH_3)OSi(CH_3)(OC_4H_9\text{-}n)_2 + (n\text{-}C_4H_9O)_2Si(CH_3)OSi(CH_3)(OC_4H_9\text{-}n)OSi(CH_3)(OC_4H_9\text{-}n)_2\ .$$

2. Reactions of Silanes Containing Two organic substituents and Two Functional Groups at the Silicon Atom and Oligosiloxanes with Two Organic Substituents per Unit.

$\alpha\omega$-Dialkoxyoligosiloxanes can be obtained by the partial hydrolysis of dialkoxydialkylsilanes or $\alpha\omega$-dialkoxyoligosiloxanes, by the esterification of $\alpha\omega$-dichlorooligosiloxanes, by homo- and hetero-functional condensation of the corresponding monomers or oligomers, and also by the hydrosilylation of the corresponding unsaturated compounds.

Dialkoxydialkylsilanes are less reactive than the corresponding dialkyldichlorosilanes and are more difficult to hydrolyse. Nevertheless, on heating in aqueous alcohol in the presence or absence of catalysts, they form the corresponding $\alpha\omega$-dialkoxyoligosiloxanes and a certain amount of cyclosiloxanes and polysiloxanes. Thus, when diethoxydiethylsilane was heated (10 h at 90°C) in alcohol with different amounts of water, the oligomers $C_2H_5O[(C_2H_5)_2SiO]_nC_2H_5$ with $n = 4$ (30.3%), $n = 7$ (76.3%), $n = 8$ (74.8%), and $n = 70$ (73.1%) were isolated[93].

$\alpha\omega$-Diethoxyoligo(chloromethyl)methylsiloxanes with $n = 2$, 3, or 4 were obtained by hydrolysing (chloromethyl)diethoxymethylsilane with a small amount of water (in alcohol) or by the esterification of dichloro(chloromethyl)methylsilane (10 h at 75–80°C)[94]. Partial hydrolysis of dibutoxydipentylsilane yields the oligomers $C_4H_9O[(C_5H_{11})_2SiO]_nC_4H_9$ with $n = 1-5$,[95] and that of di-t-butoxymethylphenylsilane gives t-$C_4H_9O[CH_3(C_6H_5)SiO]_nC_4H_9$-t ($n = 1-5$)[96]. 1,3-Dibutoxytetramethyldisiloxane and 1,5-dibutoxyhexamethyltrisiloxane were isolated in very low yields (4.9 and 2.6%) from an alcoholic solution of dibutoxydimethylsilane kept for two days. Only 9.2% of the initial dibutoxydimethylsilane remained[97].

Hydrolysis of $(CH_3)_2Si(OCH_3)_2$ in the presence of a small amount of alkali as a catalyst in 20% aqueous methanol leads to the oligomers $CH_3O[(CH_3)_2SiO]_nCH_3$ ($n = 2-10$)[98], while $C_2H_5O[(CH_3)_2SiO]_nC_2H_5$ ($n = 2-11$) is formed from $(CH_3)_2Si(OC_2H_5)_2$[99–101]. Cyclosiloxanes were isolated together with the above compounds.

$\alpha\omega$-Dialkoxyoligosiloxanes can be obtained directly from dialkyldichlorosilanes. The oligomers $C_2H_5O[(CH_3)_2SiO]_nC_2H_5$ with $n = 2$ (42%), $n = 3$ (39.2%), and $n = 4$ are formed on simultaneous partial hydrolysis and esterification of dichlorodimethylsilane with 97% ethanol[102]. The analogous reaction with isopropyl alcohol gives iso-$C_3H_7O[(CH_3)_2SiO]_nC_3H_7$-iso ($n = 1-5$) in an overall yield of 65–85%,[103] and the reaction with moist n-butyl alcohol gives 1,3-dibutoxytetramethyldisiloxane and 1,5-dibutoxyhexamethyltrisiloxane[92]. The products of the esterification of dichlorodiethylsilane by methanol are the oligomers $CH_3O[(C_2H_5)_2SiO]_nCH_3$ with $n = 1-4$.[104] The reaction of dichlorodiphenylsilane with ethanol leads to 1,3-diethoxytetraphenyldisiloxane[105].

1,3-Di-n-butoxy-1,3-dimethyl-1,3-di-α-naphthyldisiloxane (37.7%) and 1,5-di-n-butoxy-1,3,5-trimethyl-1,3,5-tri-α-naphthyltrisiloxane (26.7%) were obtained by the esterification with n-butyl alcohol of the hydrolysis products of dichloromethyl-α-naphthylsilane[106]. When

the amount of alcohol is reduced by a factor of 4, the yield of disiloxane falls to 25.5% and that of trisiloxane to 4.4%, the main reaction product being $C_4H_9O[CH_3(\alpha\text{-}C_{10}H_7)SiO]_4H$ (53.3%). The corresponding 1,3-dibutoxydisiloxane was also obtained by the reaction of dichloromethyl-α-naphthylsilane with butyl alcohol (yield 11%) or with sodium butoxide (yield 5–6%). In both cases dibutoxymethyl-α-naphthylsilane is formed simultaneously in yields of 60 and 80% respectively[106]. The hydrolysis is sometimes carried out in the presence of hydrogen chloride acceptors.

$\alpha\omega$-Dimethoxyoligodimethylsiloxanes ($n = 2-6$) were isolated in 72–76% yield after partial alcoholysis of dichlorodimethylsilane and the subsequent interaction of the alkoxychlorodimethylsilane formed with $NaHCO_3$. $\alpha\omega$-Diethoxy- and $\alpha\omega$-di-isopropoxy-oligosiloxanes were obtained similarly[107,108]. $\alpha\omega$-Di-t-butoxyoligodimethylsiloxanes with $n = 1-5$ were synthesised directly by the esterification of dichlorodimethylsilane with t-butyl alcohol in the presence of pyridine[109].

$\alpha\omega$-Dialkoxyoligosiloxanes with two organic substituents per unit may be obtained by the exchange of the functional groups in the oligosiloxanes. Thus treatment of $\alpha\omega$-dichloro-oligodialkylsiloxanes with a mixture of anhydrous alcohol and pyridine in benzene leads to 1,7-diethoxyoctaethyltetrasiloxane (70%), 1,7-diethoxytetraethyltetrapropyltetrasiloxane (69%), and tetrabutyl-1,7-diethoxytetraethyltetrasiloxane (73.3%)[38].

If the formation of hydrogen chloride or its salts is undesirable, orthoformic esters may be employed instead of alcohol. The oligomers $R'O(R_2SiO)_nSiR_2OR'$ (R' = alkyl, aryl, or alkylaryl) with $n = 2-1000$ were obtained by this method[110].

$\alpha\omega$-Dialkoxyoligosiloxanes were obtained from $\alpha\omega$-dichloro-oligosiloxanes with trimethylsiloxy-groups in the main chain and CH_3OH, C_2H_5OH, $(CH_3)_2CHOH$, and C_4H_9OH: [60,61]

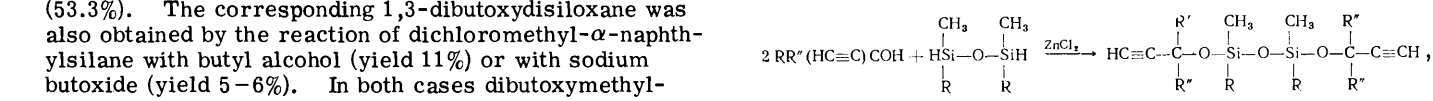
$$RO[(CH_3)_2SiO]_2SiO\{Si[OSi(CH_3)_2]_2O\}_n[OSi(CH_3)_2]_2OR \quad (n = 0,1,2,3,4)$$

and

$$RO(R')CH_3SiO\{Si[OSi(CH_3)_2]_2O\}_nSiCH_3(R')OR \quad (n = 1,2,3 \text{ etc. } R = CH_3 \text{ or } C_6H_5).$$

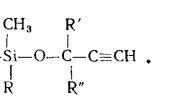
Heterofunctional condensation of dichloromethylphenylsilane with diethoxydimethylsilane, diethoxymethylphenylsilane, and diethoxyethylphenylsilane (in proportions of 1 : 2) in the presence of $FeCl_3$ leads to 1,3-diethoxy-1,1,3-trimethyl-1-phenyldisiloxane, 1,3-diethoxy-1,3-dimethyl-1,3-diphenyldisiloxane, 1,3-diethoxy-3-ethyl-1-methyl-1,3-diphenyldisiloxane, 1,5-diethoxypentamethyl-3-phenyltrisiloxane, 1,5-diethoxy-1,3,5-trimethyl-1,3,5-triphenyltrisiloxane, 1,5-diethoxy-1,5-diethyl-3-methyltriphenyltrisiloxane, 1,7-diethoxyhexamethyl-3,5-diphenyltetrasiloxane, and 1,7-diethoxy-1,3,5,7-tetramethyl-1,3,5,7-tetraphenyltetrasiloxane[111]. The redistribution of functional groups occurring in this process leads to the formation of a mixture of low-molecular-weight and high-molecular-weight condensation products, which hinders the isolation of the pure substances. Therefore the yield of tetrasiloxane does not exceed 47% and sometimes reaches only 13%. $(C_6H_5)_2Si[OSi(CH_3)_2OCH_3]_2$ was obtained by the heterofunctional condensation of diphenylsilanediol with $(CH_3)_2Si(OCH_3)Cl$.[53]

1,3-Dialkoxy-1,3-dialkyl-1,3-dimethyldisiloxanes have been synthesised by the dehydrocondensation of tertiary acetylenic alcohols with 1,3-diethyl-1,3-dimethyl- or 1,3-dimethyl-1,3-dipropyl-1,3-dihydrodisiloxanes in the presence of $ZnCl_2$ according to the mechanism[112]



where (a) R = C_2H_5 and R' = R'' = H, (b) R = C_3H_7 and R' = R'' = H, (c) R = C_2H_5, R' = H, and R'' = C_3H_7, (d) R = C_2H_5 and R' = R'' = CH_3, (e) R = R'' = C_2H_5 and R' = CH_3, (f) R = C_3H_7, R' = CH_3, and R'' = n-C_4H_9.

Under certain reaction conditions and for certain structures of the initial components, monoalkynyloxy-derivatives of tetra-alkyldisiloxanes are also formed:



1,3-Diethoxytetraethyldisiloxane and 1,5-diethoxyhexaethyltrisiloxane were obtained by heating diethoxydiethylsiloxane in an autoclave at about 300°C in the presence of $AlCl_3$ or BCl_3:[113]

$$(C_2H_5)_2Si(OC_2H_5)_2 \xrightarrow{AlCl_3} C_2H_5O[(C_2H_5)_2SiO]_nC_2H_5$$

(n = 2 or 3).

$[CH_3CH = CHOSi(C_2H_5)_2]_2O$ and $[(C_2H_5)_2SiOC(CH_3) = CHCH(CH_3)_2]_2O$ were obtained by the addition of the tetraalkyldisiloxane to acrolein or mesityl oxide[114,115].

V. METHODS OF SYNTHESIS OF $\alpha\omega$-DIAMINO-OLIGOSILOXANES

$\alpha\omega$-Diamino-oligodialkyldisiloxanes are obtained by the reaction of $\alpha\omega$-dichloro-oligodialkylsiloxanes with ammonia or amines:

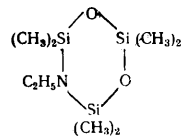
$$Cl(SiR_2O)_nSiR_2Cl + 4R'_2NH \rightarrow R'_2N(SiR_2O)_nSiR_2NR'_2 + 2R_2NH_2Cl,$$

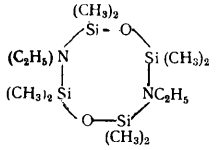
where R' = alkyl or H. Depending on the nature of the substituents at the nitrogen atom, the chain length of $\alpha\omega$-dichloro-oligosiloxanes, and the reaction conditions, $\alpha\omega$-diamino-oligosiloxanes, cyclosiloxazanes, or their mixtures may be obtained.

The initial oligomers containing up to six silicon atoms in the molecule react with an excess of ammonia to form cyclic compounds—cyclosilazanes and cyclosiloxazanes[116]. With increase of the number of silicon atoms in the chain of $\alpha\omega$-dichloro-oligosiloxanes to 7–11, the tendency by the latter towards ring formation falls and linear $\alpha\omega$-diamino-oligodialkylsiloxanes are formed.

When an ethereal solution of an $\alpha\omega$-dichloro-oligosiloxane was added to liquid ammonia, the oligomers $NH_2[(CH_3)_2SiO]_nSi(CH_3)_2-NH_2$ with $n = 6$ (72%), $n = 7$ (58.6%), $n = 8$ (46.4%), $n = 9$ (54.8%), and $n = 10$ (45.4%) were obtained. The analogous reaction with methylamine leads to 1,3-di(methylamino)tetramethyldisiloxane and 1,5-di(methylamino)-hexamethyltrisiloxane[117,118], which, in contrast to the corresponding amino-derivatives, do not cyclise on heating. When gaseous methylamine is passed into a solution of $\alpha\omega$-dichloro-oligodimethylsiloxanes, the cyclisation products $[Si(CH_3)_2OSi(CH_3)_2N(CH_3)]_2$ and $Si(CH_3)_2OSi(CH_3)_2N(CH_3)$ and the linear dimer $(CH_3)N[Si(CH_3)_2OSi(CH_3)_2N(CH_3)_2]_2$ are formed together with 1,3-di(methylamino)tetramethyldisiloxane (yield 40%) and 1,5-di(methylamino)hexamethyltrisiloxane (32%).

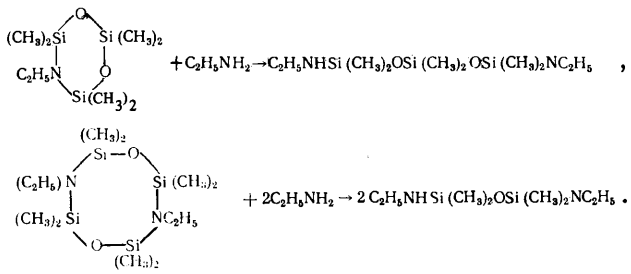
However, when the reaction is carried out at −60°C, the products are αω-di(methylamino)oligodimethylsiloxanes containing between 2 and 10 silicon atoms in yields of 51.8, 65.5, 39.8, 31.4, 21.1, 62.0, 73.3, 74.1, and 37.4% respectively[119]. Depending on the conditions, the products of the analogous reaction of methylamine may be both linear and six- and eight-membered cyclic compounds:





The latter are formed when the process is carried out in a solvent with equimolar proportions of the αω-dichloro-oligosiloxane and the amine. In the absence of a solvent and in the presence of an excess of the amine, the products are the linear oligomers $C_2H_5NH[(CH_3)_2SiO]_nSi(CH_3)_2NHC_2H_5$ with n = 1−4.[120]

It has been suggested that cyclic condensation products are formed in the initial reaction stage and undergo ring opening under the action of the excess of the amine with formation of αω-diamino-oligodimethylsiloxanes[120]:



αω-Dichloro-oligodimethylsiloxanes containing between 5 and 10 silicon atoms in the molecule form linear αω-di(ethylamino)-oligodimethylsiloxanes even in the presence of only the equimolar reactant ratio. The yields of the oligomers are 37.5% for n = 5, 30.5% for n = 6, 36.0% for n = 7, 28.6% for n = 8, 40.8% for n = 9, and 46.5% for n = 10.[121]

The reaction of αω-dichlorodimethylsiloxane with diethylamine yielded the oligomers $(C_2H_5)_2N[(CH_3)_2SiO]_nSi(CH_3)_2N(C_2H_5)_2$ with n = 2−10, which exhibit a high thermal stability. Cyclic compounds are not isolated under these conditions. The yield of the oligomers was between 30 and 60%.[121] With increase in the size of the organic substituent at the nitrogen atom, the capacity for cyclisation diminishes.

The reaction of 1,5-dichlorohexamethyltrisiloxane with n-butylamine gave 1,5-di-(n-butylamino)hexamethyltrisiloxane, which cyclises on heating only in the presence of $CuBr_2$ or $(NH_4)_2SO_4$.[54] αω-Dichloro-oligosiloxanes containing more or less than three silicon atoms in the molecule react with n-butylamine, also forming only linear αω-di(n-butylamino)oligodimethylsiloxanes with n = 1 (70.3%), n = 2 (50.2%), n = 3 (57.7%), n = 4 (50.8%), n = 5 (34.9%), n = 6 (35.8%), n = 7 (43.7%), and n = 8 (51.5%).[122]

VI. SYNTHESIS OF OLIGOSILOXANE-αω-DIOLS

1. Hydrolytic Cleavage of Cyclosiloxanes

The cleavage of oligomeric cyclosiloxanes with two organic substituents by water takes place in the presence of acid[123-125] or alkaline[126,127,129] catalysts: $(R_2SiO)_n + H_2O \xrightarrow{H^+,\ OH^-} HO(R_2SiO)_nH$. In the absence of catalysts cyclosiloxanes are cleaved by water only under severe conditions (at 250°C under pressure), which promote the formation of high-molecular-weight siloxane αω-diols[128].

Acids with a dissociation constant >6.5 × 10^{-2} (HCl, H_2SO_4, p-$CH_3C_6H_4SO_3H$) have been suggested as catalysts for the hydrolytic cleavage of siloxanes and tetrahydrofuran (THF), dimethylformamide, acetonitrile, or acetone have been proposed as solvents[123].

Thus when D_3 is cleaved with 0.05 N HCl in tetrahydrofuran, the products are about 82% of hexamethyltrisiloxane-1,5-diol, about 13% of the initial cyclosiloxane, and about 6% of an unidentified compound. Hexaphenylcyclotrisiloxane is cleaved with 0.5 N HCl in acetone to hexaphenyltrisiloxane-1,5-diol in yields up to 34%.

1,3-Dimethyl-1,3-diphenyldisiloxane-1,3-diol is obtained by the cleavage of 1,3,5-trimethyl-1,3,5-triphenylcyclotrisiloxane with an excess of potassium hydroxide in alcoholic solution with subsequent hydrolysis of the resulting siloxanolate in the presence of KH_2PO_4.[126] The yield of siloxanediol was 87%.

Ammonia and amines are also used as catalysts for the hydrolytic cleavage of cyclotrisiloxanes with six organic substituents[129]. In this case the rearrangement of siloxane bonds, observed in catalysis by strong acids or bases, is ruled out. Such catalysts make it possible to obtain virtually pure linearoligosiloxane-αω-diols with two organic substituents per unit. For example, the cleavage of 1,3,5-tri-(3,3,3-trifluoropropyl)-1,3,5-trimethylcyclotrisiloxane with a mixture of 29% ammonia solution, water, and acetone over a period of 16 h at 20°C gave mainly $HO[CH_3(CF_3CH_2CH_2)SiO]_3H$.

Acid and basic ion-exchange resins are also used as catalysts for the hydrolytic cleavage of cyclosiloxanes[130,131]. Thus in the presence of Amberlite IR-120, D_3 dissolved in acetone is converted into $HO[(CH_3)_2SiO]_nH$ with n = 3 (41%) and n = 6 (11.2%). Basic resins promote the formation of a hexamer[131].

Octamethyltetrasiloxane-1,7-diol was obtained by heating (150°C, 1,5 h) D_4 with 1% of glycerol and 0.5% of bleaching earth containing minerals of the montmorillonite group[132].

Oligosiloxane-αω-diols with two organic substituents per unit are also formed when cyclosiloxanes are cleaved with diphenylsilanediol[133] or with siloxane-αω-diols[126]: $(R_2SiO)_n + HO(R'_2SiO)_mH \rightarrow HO(R_2SiO)_n(R_2SiO)_mH$.

2. Hydrolysis of Silane with two Functional Groups at the Silicon Atom and Two Organic Substituents

A convenient method for the preparation of oligosiloxane-αω-diols is based on the capacity of Si−Cl, Si−OCOR, Si−OR, Si−NRR′, Si−H, Si−SH, Si−SR, etc. bonds in the corresponding disubstituted silanes with two organic groups and in αω-difunctional oligosiloxanes to be readily cleaved by water with formation of Si−OH bonds. Depending on the hydrolysis conditions, the latter can persist or condense further: $nR_2SiX_2 + (n+1)H_2O \rightarrow HO(R_2SiO)_nH + 2nHX$ (X = Cl, OCOR, OR, NRR′, H, SH, or SR).

The reactivity (including the reactivity with respect to water) of Si–X bonds in compounds with functional groups at the silicon atoms falls in the following sequence: Cl > OCOR > OR.[6] Usually the most readily available dichlorosilanes with two organic substituents are hydrolysed. However, during their hydrolysis hydrochloric acid appears in the reaction medium and causes the cyclisation of the siloxanediols. To avoid the formation of a large amount of cyclosiloxanes and high-molecular-weight siloxanediols, the hydrolysis is usually performed under mild conditions (at a low temperature and in the presence of a hydrogen chloride acceptor). The first member of the homologous series of the $HO[(CH_3)_2SiO]_nH$ ($n \geq 2$) oligomers—tetramethyldisiloxane-1,3-diol—was synthesised in a yield of up to 60% by the hydrolysis of dichlorodimethylsilane with a large excess of cold water (2°C) in the presence of NH_4OH (pH ~ 7) [134,135]. When gaseous ammonia is introduced, reproducible results are not always obtained owing to the difficulty of regulating the rate of its supply and the removal of the heat evolved.

Hydrogen chloride can also be neutralised by ammonium sulphate containing magnesium carbonate[136], $NH_4HCO_3(NH_4)_2CO_3$,[138] $NaHCO_3$, $Na_2B_4O_7.10H_2O$,[137] or ammonium bicarbonate carbamate ($NH_4HCO_3.NH_2CO_2NH_4$).[138] In the latter case a pH of 6–8 can be readily attained during the hydrolysis. However, the yield of tetramethyldisiloxane-1,3-diol is only 39%. A decrease of the amount of water leads to a shift of the pH of the reaction medium to the weakly acid region, which makes it possible to obtain higher oligosiloxanediols (hexamethyltrisiloxane-1,5-diol and decamethylpentasiloxane-1,9-diol).

Tetraphenyldisiloxane-1,3-diol (51%) and hexaphenyltrisiloxane-1,5-diol (18%) were obtained by the same method from dichlorodiphenylsilane. The hydrolysis of $(C_6H_5)_2SiCl_2$ with cold water gives low yields of tetraphenyldisiloxane-1,3-diol and hexaphenyltrisiloxane-1,5-diol[139]. Tetraphenyldisiloxane-1,3-diol was also obtained by the hydrolysis of $(C_6H_5)_2SiCl_2$ after which the resulting $(C_6H_5)_2Si(OH)_2$ was allowed to stand in the solvent (benzene–petroleum ether) for three days[140]. Tetramethyldisiloxane-1,3-diol is formed in a very low yield when dichlorodimethylsilane is treated with aqueous t-butyl alcohol[109].

Acid hydrolysis of dichloromethylphenylsilane results in the formation of only cyclotrisiloxanes with *cis*- and *trans*-structures[141]. On the other hand, hydrolysis in dilute ethereal solutions by aqueous alkalis yields ethylphenylsilanediol and 1,3-dimethyl-1,3-diphenyldisiloxane-1,3-diol[142].

Siloxanediols containing complex aromatic and alkyl groups at the silicon atoms have been obtained by the hydrolysis of more complicated dialkyl-, alkylaryl-, or diaryl-chlorosilanes. In this case the hydrolysis of the Si–Cl bond is difficult owing to the steric effect of the substituents at the silicon atoms. The silanediol formed in the first stage of the hydrolysis may be isolated from the reaction mixture. In order to synthesise silanediols, the reaction mixture sometimes has to be heated. Thus in the preparation of deca-*p*-tolylpentasiloxane-1,5-diol, dichlorodi-*p*-tolylsilane is hydrolysed by a mixture of water and ether, after which the ether is removed and the mixture heated to 250°C (at 1 mmHg pressure) and again hydrolysed[143]. The hydrolysis of $(p\text{-}ClC_6H_4)_2SiCl_2$ in toluene, ether, or isopentyl alcohol gives mainly tetra-(*p*-chlorophenyl)disiloxane-1,3-diol. When aqueous alkali or ammonia is employed, a mixture of di-(*p*-chlorophenyl)silanediol and tetra-(*p*-chlorophenyl)disiloxane-1,3-diol is formed. In ethereal solution only the monomeric silanediol is produced and on heating to 110°C is converted into hexa-(*p*-chlorophenyl)trisiloxane-1,5-diol.[144]

Dichloromethyl-α-naphthylsilane is hydrolysed to methyl-α-naphthylsilanediol and its low-molecular-weight condensation products $HO[CH_3-(\alpha-C_{10}H_7)SiO]_nH$.[106] Oligomers with three and four silicon atoms in the molecule have been isolated from the condensation products of ethylphenyl- and benzylethyl-silanediols[145,146].

The study of the effect of bulky alkyl groups (n-hexyl, n-octyl, iso-octyl, and isononyl) at the silicon atoms on the nature of the hydrolysis products of the corresponding dialkyldichlorosilanes[147] showed that in 34.7% hydrochloric acid only cyclic condensation products are formed. In dilute hydrochloric acid a mixture of cyclic and linear siloxanes was obtained, from which 1,3-diethyl-1,3-diiso-octyldisiloxane-1,3-diol (up to 58%), 1,3,5,7-tetraethyl-1,3,5,7-tetraiso-octyltetrasiloxane-1,7-diol (20%), and 1,3,5,7-tetrahexyl-1,3,5,7-tetramethyltetrasiloxane-1,7-diol (12.3%) were isolated.

Prolonged heating of silanediols with two organic substituents, particularly in the presence of dehydrating agents, promotes the successive formation of dimeric, trimeric, and higher oligomeric siloxane-αω-diols. The reaction takes place in steps. By altering the condensation conditions, it is possible to achieve the preferential formation of oligosiloxane-αω-diols, siloxanediols, or cyclosiloxanes[142].

Monomeric compounds R_2SiX_2 containing other functional groups X, for example X = OCOR or OR, are also used for the synthesis of oligosiloxane-α-diols. Thus di(methylvinyl)-, di(allylmethyl)-, di(phenylvinyl), di(chlorophenylvinyl), and di(allylphenyl)-siloxane-1,3-diols have been obtained in yields up to 90–98% by the hydrolysis of the corresponding diacetoxysilanes with two organic substituents[148,149].

Dimethyldi-(1-pentynyl)disiloxane-1,3-diol and di-(1-hexynyl)dimethyldisiloxane-1,3-diol were prepared by the hydrolysis of the corresponding diacetoxydialkynylsilanes with a saturated solution of sodium chloride[150,151]. The cyclosiloxane $[CH_3(CH_2)_3C \equiv CSiO]_4$ is formed at the same time, its yield increasing with temperature and the rate of addition of the acetoxysilane. The hydrolysis of alkoxysilanes with two other organic substituents is usually carried out in the presence of acid catalysts. Thus by hydrolysing diethoxyphenylvinylsilane with 0.1 *N* HCl in ethanol, 1,3-diphenyl-1,3-divinyldisiloxane-1,3-diol was obtained[152], while diethoxydiethylsilane (in 15% HCl) gave tetraethyldisiloxane-1,3-diol (yield up to 88%).[153–155]

Hydrolysis of diethoxydimethylsilane in the presence of traces of sulphuric acid resulted in the formation of tetramethyldisiloxane-1,3-diol (yield up to 66%).[156] The same compound has been obtained by the hydrolysis of dimethoxydimethylsilane[157].

Oligosiloxanediols containing pentafluorophenyl groups at the silicon atoms, $HO[(CH_3(C_6F_5)SiO]_nH$ ($n = 2$ or 4), have been obtained in 80–90% yield by the hydrolysis of dialkoxymethyl(pentafluorophenyl)silane in an alcoholic medium in the presence of acetic acid[158]. Tetramethyldisiloxane-1,3-diol is formed in the hydrolysis of hexamethylcyclotrisilthiane $[(CH_3)_2SiS]_3$ in the presence of sodium hydroxide[159]:

$$2\,[(CH_3)_2SiS]_3 + 12\,NaOH \rightarrow 3HO\,[(CH_3)_2SiO]_2H + 6Na_2S + 3H_2O\ .$$

the same compound has been obtained by the decomposition of an ethereal solution of sodium dimethylsilanediolate

with acetic acid[160,161] or with carbon dioxide[162] and also by keeping a solution of $(CH_3)_2Si(OH)_2$ in 0.001 N aqueous acetic acid[163].

Oligosiloxane-$\alpha\omega$-diols are formed in the hydrolysis of the corresponding hydrosilanes and hydrosiloxanes in the presence of silver, Ag_2O, CuO,[164] and ruthenium on charcoal[165] or when oxygen is passed through a mixture containing a hydrosiloxane, an amine, and a copper(I) salt[166]:

$$H(R_2SiO)_nSiR_2H + H_2O \xrightarrow{Ag,Ag_2O,Ru/C} HO(R_2SiO)_nSiR_2OH + H_2\ (n=0,1\ \text{etc.}),$$

$$H(R_2SiO)_nSiR_2H + O_2 \xrightarrow[CuX]{R_3N} HO(R_2SiO)_nSiR_2OH.$$

3. Hydrolysis of Terminal Functional Groups

The easiest method of synthesising pure oligosiloxane-$\alpha\omega$-diols with two organic substituents is based on the hydrolysis of the terminal functional groups in the corresponding $\alpha\omega$-disubstituted oligosiloxanes with two organic substituents:

$$X(R_2SiO)_{n-1}SiR_2X + 2H_2O \rightarrow HO(R_2SiO)_nH + 2HX\ (X=Cl, OR, OCOR\ \text{etc.}).$$

The disadvantages of the method are the necessity for a preliminary synthesis of the initial oligosiloxane and the possibility (under unfavourable reaction conditions) of side processes involving condensation (primarily cyclisation), cleavage, and rearrangement of the siloxane bonds. The effect of the conditions in the hydrolysis of $\alpha\omega$-dichloro-oligodimethylsiloxanes on the composition of the hydrolysis products has been investigated in fair detail[6,167]. Oligodimethylsiloxane-$\alpha\omega$-diols $HO[(CH_3)_2SiO]_nH$ have been obtained in high yields [$n = 2$ (88%), $n = 3$ (74%), $n = 4$ (76%), and $n = 5$ (55%)] by adding rapidly an approximately 10% etheral solution of the corresponding $\alpha\omega$-dichloro-oligodimethylsiloxane to a 5% solution of sodium hydroxide.

As in the case of dichlorodimethylsilane, hydrolysis in an acid medium leads to a mixture of linear (50%) and cyclic (50%) siloxanes. The only exception is 1,5-dichlorohexamethyltrisiloxane which yields 12% of cyclosiloxanes. By hydrolysing the corresponding $\alpha\omega$-dichloro-oligosiloxanes containing two organic substituents with a 5% solution of alkali in ether, oligodimethylsiloxane-$\alpha\omega$-diols, containing between two and nine silicon atoms in the molecule[168], oligomethylphenylsiloxane-$\alpha\omega$-diols with $n = 2-4$ [169], and also pentaethyltripropyl-, tetraethyltetrapropyl, and tetrabutyltetraethyl-tetrasiloxane-1,7-diols were obtained in yields up to 88%.[38]

When $NaHCO_3$, Na_2CO_3, and NH_4OH were used as neutralising agents, oligodimethylsiloxane-$\alpha\omega$-diols with $n = 9$ (70.9%), $n = 13$ (88.9%), and $n = 53$ (66.5%),[170] siloxanediols containing fluorinated groups at the silicon atoms $HO[CH_3(RCH_2CH_2)SiO]_nH$ (R = perfluoroalkyl containing between one and three carbon atoms; $n = 2$, 3, or 4) [171], and also the siloxanediols $RR'Si[OSi(R''R''')OH]_2$ [$R = R' = CH_3$, $R'' = R''' = C_6H_5$; R = cyclo-C_6H_{11}, $R' = CH_3$, $R'' = CH_2C \equiv CCH_3$, $R''' = CH_3$; $R'' = R''' = CH_3$, $R = C_6H_5$, $R' = CH_3$; $R'' = R''' = CH_3$, $R = C_6H_5$, $R' = CH{=}CH_2$; $R'' = R''' = CH_3$, $R = C_2H_5$, $R' = CH_3$; $R'' = R''' = CH_3$, $R = CH_2CH(CH_3)C_6H_5$, $R' = CH_3$; $R'' = R''' = CH_3$, $R = CH_2CH_2CF_3$, $R' = CH_3$; $R'' = R''' = CH_3$, $R = C_{18}H_{37}$, $R' = CH_3$; $R'' = R''' = CH_3$, R = chlorocyclohexyl, $R' = CH_3$] [53], and oligomers in which the main chain is bounded by trimethylsiloxy-groups were obtained[58,59]:

$$HO[(CH_3)_3SiO]_2SiO\{Si[OSi(CH_3)]_2O\}_nSi[OSi(CH_3)_2]_2OH$$

and

$$HO(R)CH_3SiO\{Si[OSi(CH_3)_3]_2O\}_nSiCH_3(R)OH\ (R=CH_3, C_6H_5;\ n=1, 2, 3, \text{etc.})$$

1-Methyl-1,3,3-triphenyldisiloxane-1,3-diol may be obtained by the hydrolysis of 1,3-dichloro-1-methyl-1,3,3-triphenyldisiloxane in the presence of aniline[16]. Hydrolysis of an ethereal solution of 1,3-dichlorotetraphenyldisiloxane and 1,5-dichlorohexaphenyltrisiloxane in an aqueous dioxan medium (molar ratio dichlorosiloxane: water = 2.1 or 1.5 : 1) yields tetraphenyldisiloxane-1,3-diol (92%) and hexaphenyltrisiloxane-1,5-diol (64%) [19].

Two stereoisomers [meso- and (±)-forms] of 1,3-dimethyl-1,3-diphenyldisiloxane-1,3-diol were obtained by the hydrolysis of a diastereoisomeric mixture of 1,3-dichloro-1,3-dimethyl-1,3-diphenyldisiloxane with 10% aqueous ammonia in ether[15].

Oligosiloxane-$\alpha\omega$-diols with two organic substituents can also be obtained by the hydrolysis of the corresponding $\alpha\omega$-dialkoxyoligosiloxanes with two organic substituents per unit. However, their hydrolysis is much slower than that of the corresponding $\alpha\omega$-dichloro-oligosiloxanes with two organic substituents per unit and in many cases requires the use of acid and basic catalysts. For example, tetraphenyldisiloxane-1,3-diol is formed on hydrolysis of ethoxytetraphenyldisiloxane with 8% hydrochloric acid in toluene or pentyl alcohol[105]. However, oligodimethylsiloxane-$\alpha\omega$-diols with $n = 1-5$ has been obtained by the hydrolysis of $\alpha\omega$-diethoxyoligodimethylsiloxanes in a neutral medium[172].

$\alpha\omega$-Diacetoxyoligosiloxanes with two organic substituents per unit can be used to synthesise siloxanediols[173,174]. They are more reactive than alkoxyoligosiloxanes and form on hydrolysis acetic acid, which does not exhibit a powerful condensing activity like that of hydrogen chloride liberated on hydrolysis of $\alpha\omega$-dichloro-oligosiloxanes. While the hydrolysis of the latter must be carried out under very mild conditions (tenfold dilution of the oligomers with the solvent and the use of a hydrogen chloride acceptor), $\alpha\omega$-diacetoxysiloxanes can be hydrolysed in the absence of solvents and in the absence of an acetic acid acceptor. However, in some cases hydrolysis in the presence of $CaCO_3$ proceeds more smoothly. $HO[(CH_3)_2SiO]_nH$ with $n = 2-5$ (yield 60–90%) and $HO[CH_3(CF_3CH_2CH_2)SiO]_nH$ with $n = 2-4$ (yield 60–80%) have been obtained.

In the hydrolysis of $\alpha\omega$-diacetoxydimethyloligosiloxanes in the presence of CH_3COOH acceptors ($CaCO_3$, NH_4HCO_3, NH_4OH) the highest yields are achieved when $CaCO_3$ is employed. With increase of the basicity of the CH_3COOH acceptor, the cyclosiloxanes D_3 and D_4 appear in the hydrolysis products.

In contrast to $\alpha\omega$-diacetoxydimethylsiloxanes, $\alpha\omega$-diacetoxyoligo-(3,3,3-trifluoropropyl)methylsiloxanes are converted more smoothly into the corresponding siloxanediols when stronger bases, for example sodium hydroxide, are employed as CH_3COOH acceptors. This is evidently associated with the steric effect of the 3,3,3-trifluoropropyl groups, which prevent the condensation of the siloxanediol formed and at the same time hinder the hydrolysis of the acetoxy-groups.

The hydrolysis of $C_6H_5RSi[OSiR'R''(OAc)]_2$ ($R = C_6H_5$, $R' = R'' = CH_3$; $R = CH_3$, $R' = R'' = C_6H_5$; $R = C_6H_5$, $R' = C_6H_5$, $R'' = CH_3$) in ethereal solution in the presence of sodium carbonate has been described[53].

4. The Anhydrocondensation Reaction

Oligosiloxane-$\alpha\omega$-diols with two organic substituents per unit are formed in the anhydrocondensation of silanediols with two organic substituents[175,176]: $n R_2Si(OH)_2 \rightarrow HO(R_2SiO)_nH + (n-1)H_2O$, or in the anhydrocondensation of lower oligodialkylsiloxane-$\alpha\omega$-diols:

$$HO(R_2SiO)_nH + HO(R'_2SiO)_nH \rightarrow HO(R_2SiO)_n(R'_2SiO)H + H_2O.$$

For example, in the thermal condensation of diphenylsilanediol, hexaphenyltrisiloxane-1,5-diol was isolated[175]. On heating to 200°C, hexamethyltrisiloxane-3,3-diol is converted into the corresponding di- and tri-siloxane-$\alpha\omega$-diols in which the silicon atoms in the main chain are linked to trimethylsiloxy-groups[176]:

$$[(CH_3)_3SiO]_2Si(OH)_2 \rightarrow HO\{[(CH_3)_2SiO]_2SiO\}_nH \ (n=2 \text{ or } 3)$$

VII. PREPARATION OF DISODIUM SALTS OF OLIGOSILOXANE-$\alpha\omega$-DIOLS

Disodium (or dipotassium salts) of oligosiloxane-$\alpha\omega$-diols with two organic substituents per unit are readily obtained by the cleavage of siloxanes containing two organic substituents with sodium (or potassium) hydroxide: $(R_2SiO)_n + 2MOH \rightarrow MO(R_2SiO)_nM + H_2O$ (M = Na or K). They are usually formed in as hydrates containing between two and five water molecules, which can be removed by heating in a vacuum.

As early as 1914,[161] salts containing as many silicon atoms in the molecule as the initial cyclosiloxane were obtained by the cleavage of hexaphenylcyclotrisiloxane and octaphenylcyclotetrasiloxane with 3% solutions of sodium hydroxide or potassium hydroxide. When the product of the hydrolysis of dichlorodimethylsilane was cleaved with approximately 50% aqueous sodium hydroxide, disodium salts of tetramethyldisiloxane-1,3-diol and octamethyltetrasiloxane-1,7-diol were obtained[177]. Such reactions are usually carried out in the presence of alcohol. Thus, by cleaving the corresponding cyclosiloxanes with sodium hydroxide in methanol, the salts $NaO[(CH_3)_2SiO]_2Na.5H_2O$, $NaO[CH_3(C_6H_5)SiO]_3Na.4H_2O$,[178] and also the anhydrous salts $NaO[(CH_3)_2SiO]_2Na$, $NaO[CH_3(C_6H_5)SiO]_2Na$,[179] $NaO[CH_3(C_6H_5)SiO]_nNa$ (n = 1, 2, or 3),[180] and $NaO[CH_3(C_6H_5)SiO]_nNa$ (n = 4, 8, 12, etc.)[181] were obtained. The highest yield of the salts of oligomethylphenyl- and oligoethylphenyl-siloxane-$\alpha\omega$-diols was attained by cleaving the corresponding cyclosiloxanes with a solution of sodium hydroxide in 50% aqueous ethanol[182]. The alkali metal hydroxide may be replaced by the metal oxide[182].

The cleavage of cyclosiloxanes with sodium hydroxide is reversible[179]: $(R_2SiO)_3 + NaOH \rightleftharpoons HO(R_2SiO)_3Na \rightleftharpoons NaO(R_2SiO)_3Na + H_2O$; $2HO(R_2SiO)_3Na \rightarrow NaO(R_2SiO)_6Na + H_2O$. Therefore the reaction mixture contains salts with different chain lengths, which, however, largely correspond to the amount of alkali taken and the ring size. Regardless of the proportions of the initial reactants in the alkaline cleavage of cyclosiloxanes one of the products is always the sodium salt of tetramethyldisiloxane-1,3-diol, the yield of which falls as the molar ratio NaOH : cyclosiloxane decreases[183].

Disodium salts of siloxane-$\alpha\omega$-diols with longer chain lengths can be obtained by reducing the amount of sodium hydroxide used to cleave the cyclosiloxane, which leads to the parallel occurrence of the anhydrocondensation process

$$2(R_2SiO)_n + NaOH \rightarrow 2NaO(R_2SiO)_nH \xrightarrow{-H_2O} NaO(R_2SiO)_{2n}Na$$

or the cross-linking of the low-molecular-weight oligomers by dichlorodimethylsilane[184]: $(CH_3)_2SiCl_2 + 2NaO(R_2SiO)_nNa \rightarrow (CH_3)_2Si[O(R_2SiO)_nNa]_2 + 2NaCl$. Salts containing various substituents at the silicon atoms may be obtained by the last method.

Owing to their acid properties, due to the $p_\pi - d_\pi$ interaction between the p electrons of oxygen and the $3d$ orbitals of silicon, siloxanediols can react with alkali metals, forming the corresponding salts: $HO(SiR_2O)_nH + 2M \rightarrow MO(SiR_2O)_nM + H_2$. By allowing tetra-alkyldisiloxane-1,3-diols to react with metallic sodium in xylene[153] or in liquid ammonia[185], the corresponding salts of the diols were synthesised.

The reaction with lithium proceeds similarly[186]. Magnesium and aluminium also react readily with siloxanediols, forming polyalkylmetallosiloxanes[153,187].

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The Schmidt Reaction with Ketones

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The Schmidt reaction with ketones is reviewed. Particular attention has been devoted to the mechanism and kinetics of the interaction of ketones with hydrazoic acid. The side reactions accompanying the main process and the applications of the Schmidt reaction have been indicated.
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I. INTRODUCTION

The Schmidt reaction with ketones belongs to a large group of reactions known as sextet rearrangements. A characteristic feature of these reactions is the formation of an intermediate compound with a sextet of electrons at the nitrogen atom. The reaction is interesting because of its synthetic possibilities. The problems associated with its mechanism include the behaviour of weak bases in strongly acidic media, the characteristics of the reactivity of carbonyl compounds, the capacity of substituents to migrate, and some others. The Schmidt reaction is also a convenient model for the investigation of acid-catalysed processes.

The method is suitable for the preparation of substituted amides, tetrazoles, and ureas which are not otherwise available; some of these compounds exhibit high biological activity and have practical applications[1,2].

Numerous studies have been made on the Schmidt reaction and these have been reviewed by Wolff[3] and Smith[4] who describe the experimental data obtained up to the end of 1962. This review takes into account certain studies which were published later, particularly the recent kinetic investigations, and in this connection the mechanism of the reaction is considered in greater detail.

II. MECHANISM OF THE SCHMIDT REACTION WITH KETONES

1. Overall Characteristics of the Reaction and Its Mechanism according to Smith[4]

The rearrangement of carbonyl compounds under the influence of hydrazoic acid in the presence of acid catalysts was discovered by Schmidt in 1923.[5] It was found that carboxylic acids are converted into amines, ketones into amides, and aldehydes into nitriles and formamides:

$$RCOOH + HN_3 \xrightarrow{H^+} R\,NH_2 + CO_2 + N_2\,, \quad (1)$$

$$RCOR' + HN_3 \xrightarrow{H^+} RNHOCR' + RCONHR' + N_2\,, \quad (2)$$

$$RCHO + HN_3 \xrightarrow{H^+} RCN + RNHOCH + N_2\,. \quad (3)$$

In the presence of an excess of hydrazoic acid, tetrazoles, aminotetrazoles, and ureas are formed from ketones:

$$RCOR + 2HN_3 \rightarrow R{-}N{=}\underset{\underset{N}{\|}}{C}{-}R\,, \quad (4)$$

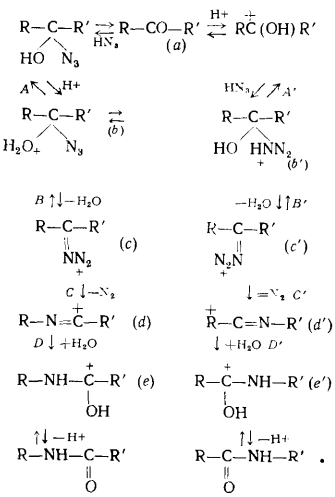
$$RCOR + 3HN_3 \rightarrow R{-}NH{-}\underset{\underset{N}{\|}}{C}{-}N{-}R\,, \quad (5)$$

$$RCOR + 2HN_3 \rightarrow RNHOCNHR\,. \quad (6)$$

Schmidt postulated that the reaction involves the cleavage of hydrazoic acid into an imino-radical [NH] and nitrogen. The imino-radical forms with the carbonyl compound an adduct, which isomerises directly to the reaction products or is converted into an oxime with subsequent Beckmann rearrangement[6]:

$$RCOR + [NH] \rightarrow \left[\begin{array}{c} N \\ | \\ R{-}C{-}R \\ | \\ OH \end{array}\right] \text{ or } \left[\begin{array}{c} R{-}C{-}R \\ \| \\ NOH \end{array}\right] \rightarrow RCONHR\,. \quad (7)$$

However, in later studies by other investigators it was shown that this hypothesis is erroneous. Modern hypotheses concerning the mechanism of the Schmidt reaction have been put forward by Oliveri–Mandala[7], Hurd[8], Sanford et al.[9], and Newman and Gildenhorn[10]. The results of these studies and his own investigations have been reviewed by Smith[11]. Taking into account certain modifications introduced in subsequent years by Smith[4], the mechanism of the Schmidt reaction in ketones can be represented as follows:



(8)

Regardless of the pathway (*A* or *A'*) followed by the rearrangement, the first reaction stage is always the interaction of the carbonyl compound (in a free or protonated form) with hydrazoic acid, which leads to the azidohydrin (*b*). Subsequent dehydration leads to the iminodiazonium ion (*c*).

As a result of the sp^2 hybridisation of the central carbon atom, the iminodiazonium ion can assume two conformations—*syn*- and *anti*-(*c* and *c'*). The assumption of the existence of two conformers of the iminodiazonium ion accounts for the formation of two isomeric amides from asymmetric ketones. The loss of nitrogen by the iminodiazonium ion is accompanied by the migration of the substituent (R or R') in the *anti*-position in relation to the diazo-group. The iminocarbonium ion (*d*) arising under these conditions interacts with water or with any other nucleophilic agent, forming the reaction products.

The mechanism [Eqns. (8)] proposed above explains satisfactorily the principal features of the reactions of ketones with hydrazoic acid although cases are known which do not fit these concepts. A detailed examination of the reaction mechanism is best made by examining the individual stages of the process, beginning with the state of the reactants in the reaction medium.

2. Behaviour of Ketones and Hydrazoic Acid in Strong Acid Solutions

The commonest catalyst of the Schmidt reaction with ketones is sulphuric acid. In most cases sulphuric acid is employed in a 10–20-fold excess in relation to the carbonyl compound and serves also as the reaction medium. In this connection it is desirable to examine the behaviour of ketones and hydrazoic acid in aqueous sulphuric acid solutions.

Ketones are typical weak organic bases which are protonated in strong acid solutions at the oxygen of the carbonyl group[9]:

$$RCOR' + H^+ \rightleftarrows [RCOHR']^+ . \qquad (9)$$

The first quantitative studies on the protonation of ketones were performed by Hammett[12]. Stewart and Yates[13] determined spectrophotometrically the pK_a for a large series of substituted acetophenones and showed that the compounds investigated belong to the series of Hammett bases. However, in a later study[14] it was found that the protonation of acetophenone and certain other conjugated ketones can be satisfactorily described by the amide acidity function H_A. Benzophenones have an individual H_B acidity scale[15]. Reinvestigation of the basicity of the series of aromatic compounds recently showed that the protonation of acetophenone and benzophenone is more satisfactorily described by the H_0 Hammett function than by H_A.[16] It is believed[17] that these discrepancies are associated with the inadequate interpretation of the experimental data by different investigators. The reason for this is the insufficient rigour of the postulates adopted in the development of methods for the calculation of the ionisation ratio of the bases.

The protonation of aliphatic ketones has been less well studied. It has been found that the ionisation constants of their conjugate acids are mainly in the range $pK_a = -6 - 8$.[18,19] The introduction of electronegative substituents into the ketone molecule greatly reduces the basicity of such compounds[20,21]. It has been shown[20,22] that the protonation of acetone, 2-butanone, 2-hexanone, and many nitroketones is satisfactorily described by the Hammett equation.

The interpretation of the protonation of ketones in terms of mechanism (9) is undoubtedly a simplification and does not reflect all the essential features of the process. Hauldna and coworkers[23–25] believe that the following equilibria are characteristic of certain ketones in solutions of strong inorganic acids:

$$S \cdot sH_2O + H^+ xH_2O \rightleftarrows S\cdots H^+ \cdot nH_2O + (s + x - n)\,H_2O ,$$
$$S\cdots H^+ nH_2O \rightleftarrows SH^+ + nH_2O , \qquad (10)$$

where S is the base (ketone). Consequently the results obtained in the study of the protonation of aliphatic ketones refer to equilibrium (10) and not (9).

In many cases there are data confirming these hypotheses. At the same time the results of the study of the activity coefficients of 2-butanone in sulphuric acid obtained by the same investigators[26] are inconsistent with this approach.

Eqn. (9) altogether fails to take into account the effect of the solvent. There is reason to believe[27] that both forms of ketones (S and SH^+) are hydrated and the protonation process may be represented as follows:

$$S \cdot bH_2O + H^+ xH_2O \rightleftarrows SH^+ \cdot mH_2O + (b + x - m)\,H_2O . \qquad (11)$$

Evidently, the final solution of this problem requires combined studies on the protonation of ketones and the kinetics of their acid-catalysed reactions.

Hydrazoic acid is a weak inorganic acid which is protonated in strongly protogenic systems:

$$HN_3 + H^+ \rightleftarrows [H_2N_3]^+ , \qquad (12)$$

$$[H_2N_3]^+ + H^+ \rightleftarrows [H_3N_3]^{2+} . \qquad (13)$$

The basicity of hydrazoic acid has been investigated by partition in sulphuric acid[28] and it has been found that the partition coefficient and hence the activity coefficient of the non-protonated form of hydrazoic acid remain constant as the concentration of sulphuric acid is varied from 25 to 40%. A sharp change in the partition coefficient was observed only in approximately 80% sulphuric acid, which is believed[28] to be due to the protonation of hydrazoic acid. The ionisation constant of $[H_2N_3]^+$ was calculated with the aid of the Hammett equation and proved to be $pK_A = -6.9$†. The anomalous variation of the partition coefficient in sulphuric acid at higher concentrations (>95%) made it impossible to characterise the second protonation process of hydrazoic acid in terms of Eqn. (13). An approximate value $pK_A = -10.9$† was adopted[30] for $[H_3N_3]^{2+}$.

It should be noted that evidence for the applicability of the function H_0 in this case is at present unavailable. Therefore the equilibrium constants obtained may not be the thermodynamic values. Here it would be useful to investigate the kinetics of the acid-catalysed reactions involving hydrazoic acid, for example the Schmidt reaction.

Sometimes hydrochloric, polyphosphoric, trichloroacetic, and trifluoroacetic acids are employed as catalysts of the Schmidt reaction. The reactions of ketones and hydrazoic acid in such media are analogous to those in sulphuric acid. However, here solvation effects play a greater role: in media of low acidity there is a possibility of the formation of a hydrogen-bonded complex of the carbonyl compound with the medium.

When the Schmidt reaction is catalysed by Lewis acids, the reaction species is probably the complex formed by the interaction of the ketone with the aprotic acid[24].

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† The values of H_0 are based on Vinnik's data[29].

The Schmidt reaction is sometimes carried out in the presence of inert solvents (chloroform, benzene) immiscible with sulphuric acid. Under these conditions, the interaction evidently takes place in an acid layer or at the interface between two phases. These features may have a definite influence on the mode of reaction.

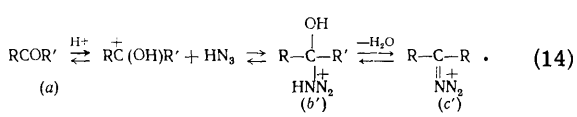
Thus one may suppose that the reactive species in the Schmidt rearrangement is the protonated form of the ketone or its complex with the acid. However, it would be incorrect to rule out completely the involvement in the reaction of the non-protonated form of the carbonyl compound, particularly for ketones with a high reactivity.

3. Addition of Hydrazoic Acid to the Carbonyl Group

The principal characteristics of the addition of nucleophilic reagents to the carbonyl group in the case of acid catalysis have been examined in reviews[31,32]. The available literature data on the Schmidt reaction suggest that these characteristics refer also to the addition of hydrazoic acid to ketones.

As shown above, when ketones are dissolved in aqueous sulphuric acid solutions with a sufficiently high acidity, they are protonated. This leads to an appreciable increase of the polarity of the carbonyl group and promotes the addition of a nucleophilic agent such as hydrazoic acid. In solutions where the carbonyl compound is not protonated, the Schmidt reaction takes place with difficulty.

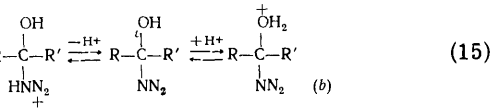
However, in media with a high acidity ($H_0 > -9$) the rearrangement is retarded owing to a decrease of the concentration of the non-protonated form of hydrazoic acid. The interaction of hydrazoic acid with a ketone leads to the iminodiazonium ion (*c'*). The azidohydrin (*b'*) is then formed as an intermediate:



(14)

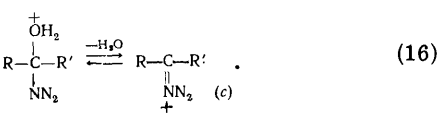
An azidohydrin of type (*b'*) was obtained and identified in the reaction of perfluorocyclobutanone with hydrazoic acid[33].

An azidohydrin with a higher energy content than the initial compound tends to regenerate the double bond. There is then a possibility both of the formation of the initial compounds and of stabilisation as a result of dehydration. Dehydration is promoted by the protolytic equilibrium



(15)

and the consequent formation of the stable iminodiazonium ion (*c*):



(16)

Compared with the hydroxycarbonium ion, the ion *c* has a lower energy content, which promotes a shift of equilibrium (14) to the right. However, dehydration can also take place by a bimolecular mechanism. In this case water or the hydrogen sulphate ion can play the role of the base.

The ease of addition of hydrazoic acid to ketones should depend on the electronic and steric properties of the substituents. Usually substituents with a $+I$- or $+M$-effect lead to an increase of the basicity of the ketone, but lowers its reactivity in relation to the nucleophilic agent. Conversely, substituents with a $-I$- or $-M$-effect reduce the basicity of the ketone, enhancing at the same time its reactivity.

The effect of substituents on the addition of hydrazoic acid to ketones and subsequent dehydration is more complex. Substituents with a $+I$- or $+M$-effect hinder the addition of the acid but facilitate the dehydration of the azidohydrin; substituents with a $-I$- or $-M$-effect have the opposite influence.

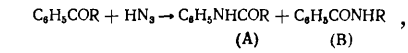
The experimental data for the reaction of ketones with hydrazoic acid are in general consistent with the above relations. It is known that aliphatic ketones are more reactive in the Schmidt reaction than alkyl aryl ketones, which are in turn more reactive than diaryl ketones. Since the basicity of the corresponding ketones increases in approximately the same sequence, it has been suggested that the rate of reaction of ketones with hydrazoic acid is determined by their basicity[11]. However, the attempt to account for the observed behaviour only on the basis of differences in the basicity of the ketones must be regarded as insufficiently justified. For example, certain substituted benzophenones are known to be weaker bases than aliphatic ketones[34].

Steric factors play a major role in the reaction of ketones with hydrazoic acid. In this sense, the accessibility of the positively charged carbon atom of the protonated carbonyl group is important. Although there are no systematic quantitative data on the effect of the structure of the carbonyl compound on the rate of the Schmidt reaction, it is known that sterically hindred ketones, such as t-alkyl ketones and *ortho*-substituted benzophenones react more slowly than straight-chain dialkyl ketones and unsubstituted diphenyl ketones[4].

4. Stereochemistry of the Reaction

The iminodiazonium ion formed as a result of the dehydration of the azidohydrin is capable of isomerisation of the same type as that observed in oximes [see mechanism (8)]. The contents of the *syn*- and *anti*-isomers in the equilibrium mixture are determined by the reaction conditions and also by steric and electronic factors. The assumption of the existence of geometrically isomeric forms of the iminodiazonium ion is exceptionally important, since it explains the formation of isomeric amides from asymmetric ketones. The problem has been analysed by Smith and coworkers[35-37]. In 1950 Smith and Horwitz[35] observed that the same ketones give a mixture of amides with the same content of isomers both in the Schmidt reaction and in the Beckmann rearrangement[38]. This enabled them to postulate a similarity of the equilibrium proportions of the isomeric oximes and the stereoisomeric forms of the iminodiazonium ion.

It has been shown for alkyl phenyl ketones and benzophenones[35] that the proportions of the amides formed are greatly influenced not by the electronic but by the steric properties of substituents. Thus in the reaction of alkyl phenyl ketones with hydrazoic acid



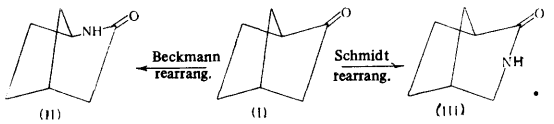
(17)

where R = CH_3, C_2H_5, or $CH(CH_3)_2$, the ratio of the

isomeric forms A/B is 95/5, 85/15, and 50/50 respectively. At the same time isomeric amides in proportions close to 1 : 1 are always formed from the benzophenones p-$RC_6H_4COC_6H_5$, where R = CH_3, C_2H_5, Cl, NO_2, or OCH_3, regardless of the nature of the substituent.

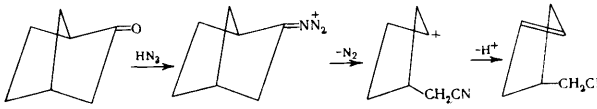
Thus the type of migration of the substituents in asymmetric ketones is in most cases satisfactorily described by an empirical rule according to which the most bulky substituent, occupying the *anti*-position in relation to the diazo-group in the iminodiazonium ion, migrates.

Similar relations hold also for many aliphatic and acyclic ketones. Thus Schechter and Kirk[39] showed for α-substituted cyclohexanones and cycloheptanones that in such ketones the reaction takes place preferentially on the substituted side of the ring. Similar observations have been made for bicyclic ketones[40] and for open-chain ketones[41]. However, in norcamphor and cyclopentanocamphor, migration from the unsubstituted side of the ring is observed[42]. At the same time the Beckmann rearrangement of the oximes of these ketones is accompanied by the formation of lactams with the "normal" structure:



(18)

It should also be noted that the yields of the corresponding amides in the Schmidt reaction are about 30%. Possibly the absence from the reaction products of the lactam (II) is associated with the formation of an unsaturated derivative of acetonitrile according to the mechanism

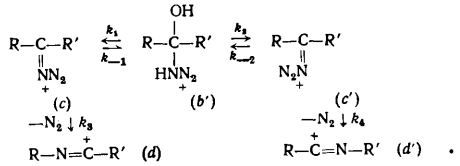


(19)

Remarkable relations have been observed for phenylalkyl ketones $C_6H_5(CH_2)_nCOCH_3$.[10,11] Acetophenone (n = 0) gives a C_6H_5/CH_3 migration ratio of 95/5, phenylacetone (n = 1) gives $C_6H_5CH_2/CH_3$ = 50/50, benzylacetone (n = 2) gives $C_6H_5(CH_2)_2/CH_3$ = 95/5, and 5-phenyl-2-pentanone gives $C_6H_5(CH_2)_3/CH_3$ = 80/20; this type of variation is probably continued with ketones having n = 4 and 5.

In most cases N-substituted acetamides are formed from alkyl methyl and aryl methyl ketones. Two cases are known where preferential migration of the methyl group was observed: N-methylcinnamide and N-methylcyclopropanecarboxamide are formed from benzylideneacetone[43] and cyclopropyl methyl ketone[44]. Extremely interesting results were obtained in a study of the isomeric ratio of the amides formed from *ortho*-substituted benzophenones[37,45] (Table 1). Contrary to expectation, it was found that these compounds do not obey the empirical rule of the preferential migration of the more bulky substituents. Similar deviations have been observed also for 2-substituted fluorononones[46].

According to the mechanism of reaction (8), two isomers of an iminodiazonium ion are formed from a protonated azidohydrin:



(20)

If the energy barrier to the $c \rightarrow d$ rearrangement is lower or comparable to that in the interconversion of the iminodiazonium ions c and c', the ratio of the resulting amides is mainly influenced by the $c \rightleftharpoons c'$ equilibrium. When the energy barrier to the rearrangement is higher, one must expect (according to the Curtin–Hammett principle[47]) that the ratio of the amides will be determined by the difference between the energy barriers to the $c \rightarrow d$ and $c' \rightarrow d'$ rearrangements.

This conclusion follows also from kinetic considerations[47,48]. If the rearrangement (k_3 and k_4) is faster than the interconversion of the isomers c and c', one can write

$$\begin{aligned} d(c)/dt &= k_1(b) - k_3(c)\,, \\ d(c')/dt &= k_2(b) - k_4(c')\,, \\ d(d)/dt &= k_3(c) = k_1(b) - d(c)/dt\,, \\ d(d')/dt &= k_4(c') = k_2(b) - d(c')/dt\,. \end{aligned} \qquad (21)$$

After integration of the last two equations and division of one by the other, we have

$$\frac{(d)}{(d')} = \frac{k_1\int(b)/dt - (c)}{k_2\int(b)/dt - (c')}\,. \qquad (22)$$

This ratio will be equal to k_1/k_2 and k_1k_3/k_2k_4 at $t = \infty$ and $t = 0$ respectively.

Table 1. Ratios of the isomeric amides from *ortho*-substituted benzophenones[45].

Substituent	$C_6H_5NHCOAr/ArNHCOC_6H_5$, %	Substituent	$C_6H_5NHCOAr/ArNHCOC_6H_5$, %
CH_3	78:22	Br	82:18
C_2H_5	78:22	CH_3	50:50
$(CH_3)_2CH$	82:18	NO_2	30:70
Cl	75:25	COOH	3:97

If the slow stage is the rearrangement, the ratio of the amides should be determined by the energy barriers to the $c \rightarrow d$ and $c' \rightarrow d'$ rearrangements and not the thermodynamic stabilities of compounds c and c'. Indeed, according to Eqn. (20) the equilibrium $c \rightleftharpoons c'$ is described by the product k_1k_2/k_2k_1 and the concentration ratio of d/d' is determined as $(k_1k_2/k_2k_1)k_3k_4$. Having denoted the first multiplier by K, we find that the concentration ratio $d/d' = Kk_3/k_4$.

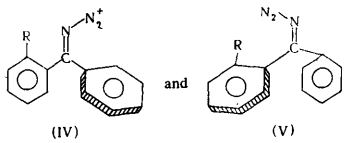
Thus the slower are the rearrangement stages with the constants k_3 and k_4 compared with the rates of interconversion of the iminodiazonium ions (k_1, k_2, k_{-1}, and k_{-2}), the most important will be the electronic factors influencing the tendency of the substituent to migrate. Under these conditions, the thermodynamic equilibrium between c and c' will be correspondingly less important.

However, the extreme cases described will hardly occur in a "pure" form. The ratio of the amides formed is more likely to be affected by all the factors enumerated. Only some of them will of course be decisive. Smith and Antoniades analysed these factors[37].

The difficulty of interpreting the available data consists in the fact that the relations applicable to one series of ketones need not necessarily obtain in another series. This last factor is evidently associated with a possible change in the rates of individual stages as a function of the nature of the ketone and with the competing effect of electronic and steric factors on the structure of the iminodiazonium ion.

As an example, one may refer to the "anomalous" behaviour of *ortho*-substituted benzophenones, in which preferential migration of the unsubstituted phenyl ring has

been observed. At the same time *ortho*-substituted acetophenones give rise to aryl migration products. Smith and Antoniades gave a convincing explanation of this phenomenon.[37] In benzophenones only one phenyl ring is conjugated with the carbonyl group, which leads to the breakdown of the coplanarity of the system. The iminodiazonium ion derived from such compounds can exist as two steric isomers (IV) and (V):



(23)

If the *ortho*-substituent promotes the conjugation of the substituted phenyl group to the carbonyl group, conformation (IV) predominates and preferential migration of the *ortho*-substituted phenyl ring is observed. When the substituent does not have an appreciable effect on the capacity of the phenyl group for conjugation, conformation (V) predominates and the migration of the unsubstituted phenyl ring is significant.

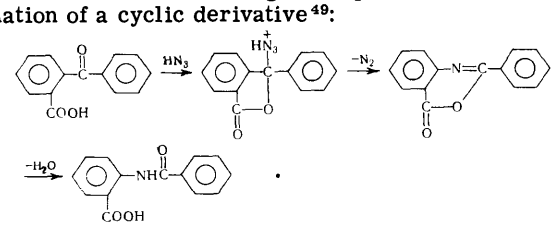
Table 2. Ratios of the isomeric amides (phenyl/substituted phenyl) from benzophenones as a function of the concentration of sulphuric acid[50].

Compound	H_2SO_4	
	88 wt.%	90 wt.%
para-Substituted benzophenones	1:1	1:1
m-Nitrobenzophenone	1:2.16	1:5.02
m-Chlorobenzophenone	1:1.12	1:3.06
m-Methylbenzophenone	0.98:1	7.00:1
p-Methyl-3,5-dinitrobenzophenone*	1.32:1*	0.27:1*

*p-Tolyl/3,5-dinitrophenyl.

The effect of electronic and steric factors on the conjugation of the substituted phenyl group is clearly shown in ketones such as *o*-ethyl- and *o*-methoxy-benzophenones. The ethyl and methoxy-groups are sterically almost equivalent, but the methoxy-group is more effectively conjugated with the phenyl ring. This difference has a marked effect on the migration ratio. The corresponding anilide is mainly formed from *o*-ethylbenzophenone, while *o*-methoxyphenone gives a 1 : 1 mixture of amides[45].

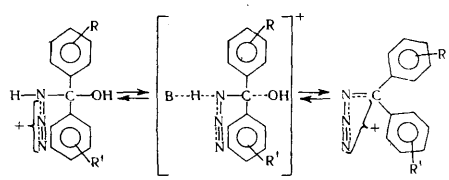
The behaviour of *o*-carboxy-, *o*-nitro-, and *o*-phenylbenzophenones, which exhibit a preferential migration of the substituted aryl group, becomes understandable if it is assumed that the rearrangement proceeds via the formation of a cyclic derivative[49]:



(24)

In many cases the isomeric composition of the mixture of amides formed from asymmetric ketones is influenced significantly by the reaction conditions (temperature and nature of the medium). It has been established that an increase of reaction temperature leads to a change of the ratio of isomeric amides towards an increase of the fraction of the isomer obtained in a smaller amount at a lower temperature[37,39].

Interesting results were obtained by Brackenridge[50] in a study of the effect of the concentration of sulphuric acid on the ratio of isomeric amides in the case of substituted benzophenones and aryl pyridyl ketones (Table 2). The results in Table 2 show that, on increase of the concentration of sulphuric acid from 88 to 99%, there is a sharp change in the migration ratio. Such considerable changes are evidently associated with an increase of the polarity of the medium on passing to more concentrated acid. This assumption may be made on the basis of the following considerations. The dehydration of the azidohydrin *b* proceeds via the transition state in scheme (25):



(25)

where B = H_2O or HSO_4^-. The degree of polarity of the transition state depends on the nature of the substituent and the position of the substituted phenyl ring in relation to the diazo-group. The transition state will be more polar when the *meta*-substituted phenyl ring (with an electronegative substituent) is in the *anti*-position with respect to the diazo-group. The transition state will be less polar when the *meta*-substituted phenyl ring (with an electron-donating substituent) is in the *syn*-position. The rate of dehydration of the azidohydrin depends more on the polarity of the solvent the greater the polarity of the transition state. Consequently, with increase of the polarity of the medium (increase of the concentration of sulphuric acid), the reaction will proceed via a polar transition state. As a result, there is a considerable change in the ratio of the isomeric amides.

Para-substituted benzophenones are almost insensitive to the effect of the medium, since substituents in the *para*-position do not have such a significant influence on the polarity of the transition state. An analogous change in the ratio of isomeric amides was observed by Tomita et al.[51] for 1-indanones and 1-tetralones when sulphuric acid was replaced by trichloroacetic acid.

In general, the problems of the stereochemistry of the Schmidt reaction are fairly complex. The earlier hypothesis of the similarity of the ratio of isomeric amides in the Schmidt reaction and in the Beckmann rearrangement proved to be very approximate when more extensive studies were made. In many cases, particularly for ketones with a complex structure[52,53], it is impossible to predict the mode of reaction. Each year an increasing amount of data accumulates, indicating the breakdown of the rules elaborated previously and further studies are therefore necessary for the solution of this problem.

5. Reaction Kinetics

The kinetics of the Schmidt reaction of ketones have been inadequately investigated. The reason for this is evidently the considerable difficulties of a quantitative study of such complex processes. A systematic investigation of the kinetics of the Schmidt reaction was only undertaken in recent years.

When the rate of reaction of certain ketones with hydrazoic acid was measured in hydrochloric and sulphuric acids, it was shown that the reaction has an overall second order and is of first order with respect to each component[54]. The expression for the rate of the process includes the acidity of the medium: $d(N_2)/dt = kh_0[HN_3]$ [ketone]. Thus the early observations of the dependence of the rate of reaction on the concentration of the acid (catalyst) were confirmed.

It has also been established that the more basic ketones react at a higher rate. On this basis, attempts were made to relate the activity of ketones to their basicity. Fichel et al.[55] studied the kinetics of the reactions of various acetophenones with hydrazoic acid in aqueous sulphuric acid. The data for *meta*- and *para*-substituted acetophenones are inconsistent with the expectations based on the migration capacities of the substituents. Certain *ortho*-substituents (OH, CH_3, OCH_3) retard the reaction, while others (NO_2, Cl) accelerate it.

The changes in the entropies and enthalpies of activation indicate the existence of an isokinetic relation. To some extent these results are consistent with Howell's data[54], but they do not reveal the principal characteristics of the reaction.

The kinetics of the Schmidt reaction involving certain aromatic ketones were studied by Mirek[56,57]. The observed rate of reaction decreases for ketones with electron-donating substituents, which is in general consistent with the effect of these substituents on the position of the carbonyl group band in the infrared spectra. On this basis, the author suggested that the slow reaction stage is the addition of hydrazoic acid to the hydroxycarbonium ion. However, since the reactions investigated are heterogeneous, the results obtained should be treated with caution because the process may be influenced by additional factors.

Quite different data have been reported by Bak[58]. The rate constant for the reaction of phenanthrenequinone with hydrazoic acid decreases appreciably when the concentration of sulphuric acid increases, which is inconsistent with earlier observations. In order to resolve these contradictions, the author suggested that the reaction may involve not only free hydrazoic acid but also its protonated form ($H_2N_3^+$). He made similar assumptions also in a study of the Schmidt reaction with benzoic acid[59].

All the investigations quoted are fragmentary and unsystematic. These and other causes have hitherto precluded an appreciable advance in the understanding in the mechanism of the Schmidt reaction. Certain problems of the formal kinetics of the reaction with ketones can be conveniently examined in the simplest case where only one of the isomeric amides is formed. Here the kinetics of the process based on the suggested reaction mechanism (8) can be represented as follows:

$$A + B^+ \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} C^+ \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} D^+ \xrightarrow{k_3, -N_2} E^+, \qquad (26)$$

(a) (b) (c)

where A is non-protonated hydrazoic acid, B^+ the protonated ketone, C^+ the protonated azidohydrin (I), D^+ the iminodiazonium ion (II), and E^+ the iminocarbonium ion (III).

One of the stages—the rearrangement of the iminodiazonium ion (stage *c*) accompanied by the liberation of N_2—is undoubtedly irreversible. Under these conditions, the occurrence of the rearrangement via a many-centre mechanism or via an intermediate nitrene is kinetically equivalent. In principle, stages (*a*) and (*b*) may be reversible.

It has been shown[60] that the rates of consumption of HN_3 and of liberation of nitrogen in the reaction of 2-hexanone with hydrazoic acid in aqueous sulphuric acid solutions are equal. This implies that the concentrations of the intermediates (I) and (II) are fairly low and may be neglected. The changes in the concentrations of (I) and (II) during the reaction can also be disregarded and therefore in the treatment below the principle of the steady-state has been employed.

If the rate of the process is limited by stage (*c*), the overall rate is

$$\frac{dN_2}{dt} = -\frac{d[A]_{st}}{dt} = k_3 K_2 K_1 [A][B^+]. \qquad (27)$$

On the other hand, if stages (*b*) and (*a*) are rate-limiting, the rate is expressed by Eqn. (28) and (29) respectively:

$$\frac{dN_2}{dt} = -\frac{d[A]_{st}}{dt} = k_2 K_1 [A][B^+], \qquad (28)$$

$$\frac{dN_2}{dt} = -\frac{d[A]_{st}}{dt} = k_1 [A][B^+], \qquad (29)$$

where $[A]_{st}$ is the stoichiometric concentration of HN_3. The variation of the concentration of the protonated ketone and non-protonated hydrazoic acid with their basicity constants and with the acidity of the medium has been omitted. The experimentally observed overall second order of the reaction and the first order with respect to each component are formally consistent with the hypothesis that the slower stage may be any one of the following three: (*a*), (*b*), and (*c*).

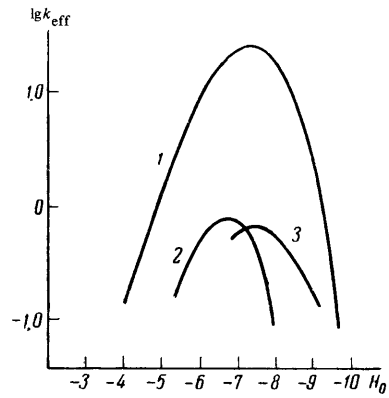


Figure 1. Variation of the logarithm of the observed (effective) rate constant for the Schmidt reaction ($\lg k_{eff}$) in sulphuric acid solutions with acidity: 1) for 2-hexanone; 2) for acetophenone; 3) for *m*-nitroacetophenone[61,62].

Certain characteristics of the mechanism of the reaction of ketones with hydrazoic acid were discovered in a study of the process over a wide range of acidities of the medium. Fig. 1 shows the observed variation of the effective rate constant for the reaction with the acidity function H_0 for 2-hexanone and for acetophenones with substituents in the phenyl ring[61,62]. With increase of the concentration of sulphuric acid, the rate of reaction rises to a maximum

and then falls. It should also be noted that the rate of the Schmidt reaction with carboxylic acids increases continuously with sulphuric acid concentration up to 96.6%,[63] which is evidence of differences in these processes.

Relations of this kind (Fig. 1) in nucleophilic addition to the carbonyl group can be accounted for either by an acid–base equilibrium of the initial reactants or by a change in the rate-limiting stage[31].

If the acid–base equilibrium of the ketone and hydrazoic acid (in the present case in sulphuric acid) is the decisive factor, the effective rate constant for the rate-limiting stage (addition) is[61,63]

$$k_{\text{eff}} = \frac{k' h_0}{K_1\left[1+\frac{h_0}{K_1}\right]\left[1+\frac{h_0}{K_2}+\frac{h_0 h_+}{K_2 K_3}\right]}, \qquad (30)$$

where k' is the true reaction rate constant, h_0 and h^+ are the acidity functions for the neutral bases and singly-charged cations respectively, and K_1, K_2, and K_3 are the basicity constants of the ketone, hydrazoic acid, and monoprotonated hydrazoic acid ($H_2N_3^+$) respectively.

Eqn. (30) is valid only when the ketone and hydrazoic acid behave as Hammett bases. Despite certain difficulties in the solution of this problem, to a first approximation one may postulate that 2-hexanone and acetophenones substituted in the phenyl ring[61,62] satisfy this requirement. The behaviour of hydrazoic acid as a Hammett indicator is assumed.

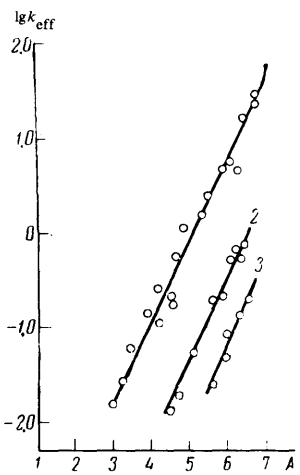


Figure 2. Correlation between $\lg k_{\text{eff}}$ and A in the Schmidt reaction: 1) for 2-hexanone; 2) for acetophenone; 3) for *m*-nitroacetophenone. $A = -H_0 - \lg(1 + h_0/K_1) - \lg(1 + h_0/K_2 + h_0 h_+/K_2 K_3)$, where H_0 is the Hammett acidity function, K_1, K_2, and K_3 are the basicity constants of the ketone, NH_3, and $H_2N_3^+$ respectively, and h_+ is the acidity for singly-charged bases.

Fig. 2 presents the observed correlations between A and k_{eff} determined by Eqn. (30).[61,62] A is the acidity function of the medium corrected for the acid–base equilibrium of the initial reactants.

The linearity of the correlations (Fig. 2) shows that, regardless of which reaction stage is rate-limiting, the reactants are first protonated in sulphuric acid and then the protonated ketone reacts with non-protonated hydrazoic acid.

The satisfactory correlation suggests that the reaction mechanism remains unchanged over a wide range of acidities of the medium. Moreover, one may postulate that the rate constant for the elementary stage does not vary, i.e. is independent of the acidity function.

The experimentally determined ranges of H_0 (Fig. 1) where the effective rate constant is a maximum agree satisfactorily with calculations by the equation

$$h_0^{\max} = \sqrt{K_1 K_2}, \qquad (31)$$

where K_1 and K_2 are the basicity constants of the ketone and hydrazoic acid respectively.

The higher absolute effective reaction rate constants for $h_0^{\max}$ correspond to the more basic ketones. This can be readily explained by the fact that for a more basic ketone, $h_0^{\max}$ is displaced towards lower acidities where the relative concentration of non-protonated hydrazoic acid is higher. The validity of the suggested mechanism (8) has been confirmed by the determination of the basicity of hydrazoic acid using a kinetic method[61]. The value obtained is relatively close to the basicity of hydrazoic acid found by a partition method[28].

The determination of the rate-limiting reaction stage is the most difficult step in the study of the mechanism of multistage processes. This problem has been examined by Smith[4] in relation to the Schmidt reaction with ketones but he did not arrive at a final solution. At the same time, determination of the rate-limiting stage of the process yields exceptionally valuable information about the reaction mechanism as a whole.

Studies on the kinetics of sextet rearrangements, which include the Schmidt reaction, showed that the rate of the process increases on introduction into the molecule of the initial compound (amide, hydroxamic acid, or carboxylic acid) of electron-donating substituents (the value of ρ in the correlation equation is negative). The absolute values of the reaction constants are fairly considerable: 2.58 for the Hoffman reaction[63], 2.51 for the Lossen reaction[64], and 1.76 for the Schmidt reaction[65] (in the last case the reaction series comprises aromatic acids).

A negative value of ρ was obtained also for the reaction of aliphatic acids with hydrazoic acid and it was shown convincingly that the rearrangement stage is rate-limiting[66]. In the absence of stages complicating the process the observed negative sign of the reaction constant ρ may be attributed to the rearrangement itself[67].

A positive reaction constant is observed only when the rate-limiting stage is nucleophilic addition to the carbonyl group[31].

The constant $\rho = +1.79$ has been determined[62] for many substituted acetophenones by correlating the logarithms of the true rate constants with Brown's σ^+ constants (Fig. 3).

The observed positive reaction constant for substituted acetophenones is in general an overall quantity comprising the reaction constants for the rate-determining and preceding stages. However, analysis shows[62] that the slowest stage probably consists in the nucleophilic addition of hydrazoic acid to the carbonyl group. The activation parameters for the Schmidt reaction with ketones are consistent with this hypothesis (Table 3). According to the theory of absolute rates, the enthalpy of a complex reaction, with the exception of cases where intermediates accumulate, may be attributed to the rate-limiting stage.

The observed values of $\Delta H^{\neq}$ are characteristic of the stage involving nucleophilic addition to the carbonyl group. Moreover, it has been shown[60] that the activation energies for the reactions of 2-hexanone with hydrazoic acid in sulphuric acid are similar in different acidity ranges. This yet again confirms that the reaction mechanism does not alter over a wide range of sulphuric acid concentrations.

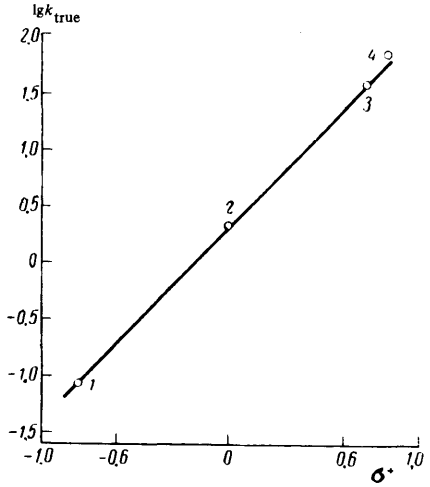


Figure 3. Correlation between the logarithm of the true rate constants for the Schmidt reaction and the electrophilic constants of the substituents:
1) *p*-methoxyacetophenone; 2) acetophenone;
3) *m*-nitroacetophenone; 4) *p*-nitroacetophenone.

The activation entropies for multistage processes are overall quantities, which gives rise to additional difficulties in their interpretation. Therefore it is useful to compare the values of $\Delta S^{\neq}$ for the Schmidt reaction involving ketones and acids. In the latter case the slowest stage is the rearrangement. A small negative value of $\Delta S^{\neq}$ can be explained by a considerable contribution due to the stage involving the liberation of nitrogen and an increase of entropy[66]. For ketones, the activation entropies are more negative, which is satisfactorily consistent with the finding that the experimental $\Delta S^{\neq}$ consist of the entropies of the protonation stage and the stage involving nucleophilic addition to the carbonyl group.

The kinetic isotope effect in the Schmidt reaction involving 2-hexanone and acetophenone has been measured[68]. In both cases the rate increases appreciably when H_2SO_4 is replaced by D_2SO_4 (Table 4). Such acceleration of the reaction is characteristic of processes with a protonation pre-equilibrium[69]. The results obtained by Koldobskii and coworkers[60-62] make it possible to resolve the apparent contradictions between the previous kinetic studies.

In their investigation of the effect of substituents on the rate of the Schmidt reaction with ketones, Fichel et al.[55] and Mirek[57] arrived at opposite results. This is evidently because the authors employed sulphuric acids of different concentrations. Fichel et al.[55] did not indicate which rate constants were employed in the calculations—the effective or true values. Evidently their conclusion is based on the effective rate constants in 67.8% sulphuric acid, which is confirmed by the plot in Fig. 1. Indeed at this concentration of sulphuric acid ($H_0 = -5.6$) the effective rate constants increase when electron-donating substituents are introduced into the ketone molecule. On the other hand, Mirek et al.[57] employed concentrated sulphuric acid (about 93%) and the sign of the effect of substituents was reversed. Correct conclusions can be arrived at only by using the true rate constants, which are independent of the acidity of the medium.

Table 3. Activation parameters and relative rates of the Schmidt reaction for substituted acetophenones[55].

Substituent	Relative rate	$\Delta H^{\neq}$	$\Delta S^{\neq}$
p-CH_3	9.50	8.26	−41.60
m-OH	1.13	—	—
H	1.00	—	—
p-Br	0.69	9.98	−36.22
m-Br	0.58	—	—
p-OCH_3	0.38	—	—
p-NO_2	0.15	14.83	−22.59
m-NO_2	0.10	—	—

The retardation of the reaction of phenanthrenequinone with hydrazoic acid as the acidity of the medium increases can be explained similarly. According to Eqn. (31), the optimum acidity (h_0^{max}) for this ketone ($pK_a = -7.8$) corresponds to $H_0 \simeq -7.4$ and since the process occurs at H_0 between −8 and −9, the rate of reaction falls as the acidity rises.

Table 4. Kinetic isotope effect (k.i.e.) in the Schmidt reaction[68].

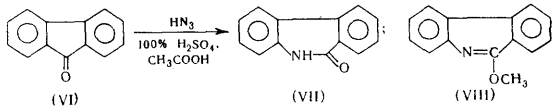
Ketone	k.i.e., litre mole^{-1} s^{-1}, 15°C		$\frac{k_D}{k_H}$
	H_2SO_4 60.5 wt.%	D_2SO_4 60.5 wt.%	
2-Hexanone	0.81	2.50	3.24
Acetophenone	0.02	0.12	6.00

Thus the available kinetic data for the Schmidt reaction involving ketones agree satisfactorily with the reaction mechanism proposed by Smith[4]. However, kinetic methods alone do not yield exhaustive information about the reaction mechanism as a whole. Here it is necessary to employ other physicochemical research techniques.

6. Other Views on the Mechanism of the Reaction of Ketones with Hydrazoic Acid

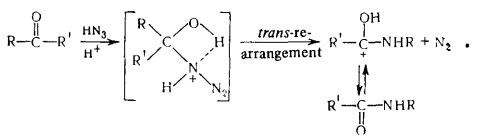
The failure in some cases of the empirical rule that the more bulky substitutent migrates preferentially in the Schmidt reaction with asymmetric ketones[44,45] led some investigators to revise the reaction mechanism proposed by Smith[4,11]. Arcus et al.[46] questioned the possibility of the existence of the iminodiazonium (*c*) and iminocarbonium (*d*) ions [mechanism (8)]. As evidence they quote data

for the Schmidt reaction with fluorenone (VI) in 100% sulphuric acid. They believe that, when an iminocarbonium ion is formed, its hydration is difficult under these conditions and dilution of the reaction mixture with an excess of methanol should lead to 9-methoxyphenanthridine (VIII):



(32)

However, the only reaction product proved to be the phenanthridone (VII). These results were interpreted as unambiguous proof of the absence of an intermediate iminocarbonium ion. As a possible alternative, they proposed a mechanism involving the formation of an intermediate four-membered ring:



(33)

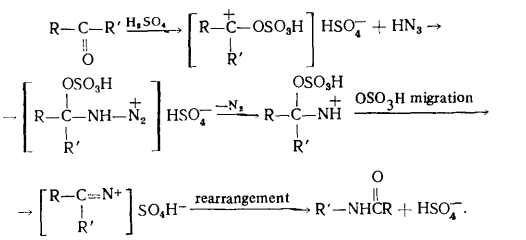
However, in subsequent studies[37,56] it was shown that the arguments put forward by Arcus et al. in favour of the mechanism with a four-membered intermediate are inadequate.

In Schmidt's early studies[70] it was already known that iminoethers are formed when ketones are treated with hydrazoic acid, provided that the reaction is carried out in alcohol. Arcus and coworkers diluted the reaction mass with alcohol only after the process had been completed, when the iminocarbonium ion had already been converted into the protonated amide as a result of hydration.

The fact that the iminocarbonium ion is nevertheless capable of being hydrated under these conditions is confirmed by the well known hydrolysis of nitriles in concentrated sulphuric acid[71,72]. Moreover, if the hydration process were thermodynamically impossible, the formation of iminocarbonium ions from amides should be expected when the latter are dissolved in sulphuric acid. However, the attempts by Newman and Deno to achieve such transformation of amides proved unsuccessful[73]. In addition it is known that, in the presence of an excess of hydrazoic acid, ketones form tetrazoles (see section III). It is not clear how such products could be formed if they were really preceded by the four-membered intermediate shown in mechanism (33).

Finally, it is noteworthy that the hydrogen bond energy is clearly insufficient for the formation of a strained four-membered ring and therefore the existence of such a structure is altogether unlikely.

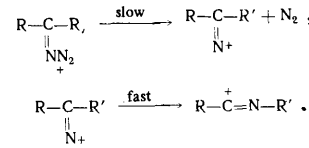
Recently Mirek[56,57] proposed the following mechanism for the Schmidt reaction with ketones:



(34)

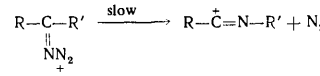
However, this mechanism has no significant advantages over the generally accepted Smith mechanism[4]. Experimental data confirming the validity of this pathway are so far lacking.

In a study of the Schmidt reaction with ketones the problem of the mechanism of the rearrangement proper is exceptionally important. According to mechanism (8), the rearrangement takes place in two stages:



(35)

On the other hand, the process can proceed via a many-centre (push-pull) mechanism with simultaneous elimination of nitrogen and migration of one of the substituents:



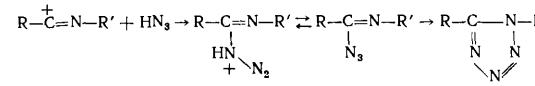
(36)

Since there is no direct proof for a particular mechanism, it is difficult to give preference to any one of them. One can only suppose, by analogy with the related Curtius, Lossen, and Hofmann reactions[74,75], that the synchronous mechanism can also operate in the Schmidt reaction.

III. CONCOMITANT REACTIONS

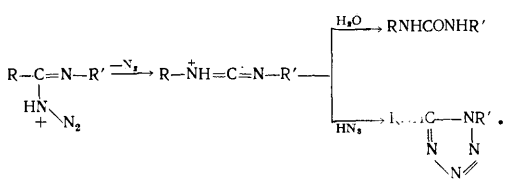
Usually the interaction of ketones with hydrazoic acid leads to the formation of amides. In certain cases, depending on the reaction conditions and the properties of the substrate, tetrazoles, aminotetrazoles, ureas, iminoethers, and certain other compounds may be obtained. Tetrazoles, which exhibit a high biological activity[76] and are used in medical practice as stimulators of cardiac activity[2], are the most important.

Tetrazoles are formed as a result of the reaction of the iminocarbonium ions *d* with an excess of hydrazoic acid:



(37)

The protonated imidoazide is capable of eliminating nitrogen with formation of a carbodi-imide which is converted into an aminotetrazole or urea as a result of secondary reactions with hydrazoic acid or water:



(38)

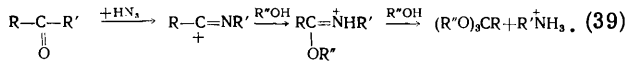
If the reaction is carried out in the presence of water, then, even if there is a large excess of hydrazoic acid, tetrazoles are always obtained in a mixture with amides. Thus benzosuberone was converted into a lactone in 82% yield when sodium azide was added slowly to a solution of the ketone in trichloroacetic acid[77]. When a mixture of the ketone and hydrazoic acid is treated with concentrated sulphuric acid, a tetrazole is formed[78]. Similarly mixtures of the corresponding amides and tetrazoles are formed from di-isobutyl-ketone[79] and cyclohexanone[80].

The formation of aminotetrazoles and urea in the Schmidt reaction takes place extremely rarely and is characteristic only of ketones such as benzophenone[81]. Tetrazoles are formed in a small amount from benzil[82].

Despite the fact that the synthesis of tetrazoles by the Schmidt reaction has found wide application, systematic

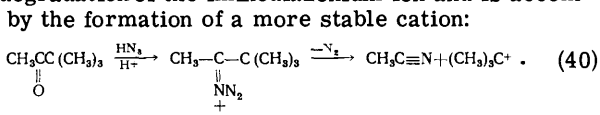
studies have not been made in this field. It is not clear how the structure of the ketone affects its capacity for conversion into a tetrazole, although such a relation undoubtedly exists. One can also suppose that the amide: tetrazole ratio (when a mixture of these products is formed) is determined by the ratio of the activities of hydrazoic acid and water and also by the acidity of the medium. Extensive kinetic studies are required for the solution of this problem.

Alcohols can enter into the reaction with the iminocarbonium ion together with water and hydrazoic acid. In this case there is a possibility of the formation of iminoethers [70]. Since in the presence of acids these substances readily undergo alcoholysis, the rearrangement products are orthoesters and amines [4]:



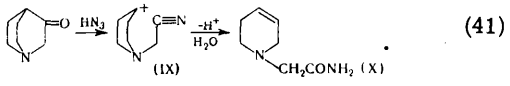
(39)

The composition of the Schmidt reaction products depends to a considerable degree on the structure of the ketone. Ketones such as pinacolone [83], pivalophenone [35], 2-n-butyl-2-phenylbutan-3-one, [84] and certain others [85] react with hydrazoic acid to form the corresponding nitriles. The formation of nitriles takes place as a result of the degradation of the iminodiazonium ion and is accompanied by the formation of a more stable cation:



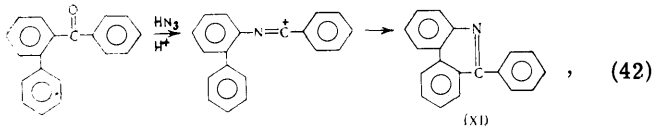
(40)

Even more far-reaching transformations are undergone by 3-quinuclidone [86,87]. In this case the carbonium ion (IX) is stabilised by the removal of a proton, which leads to the formation of an unsaturated amide (X):

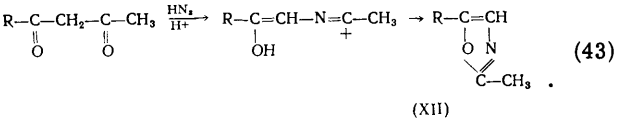


(41)

Certain ketones, for example *o*-phenylbenzophenone [45], acetylacetone, and benzoylacetone [88], give rise to cyclic products (XI–XII) as a result of the Schmidt reaction:



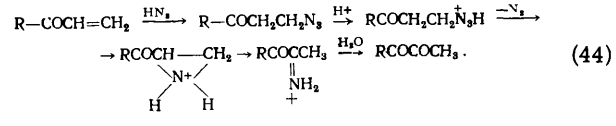
(42)



(43)

Phenylphenanthridine (XI) and oxazole (XII) are formed via an electrophilic attack by the iminocarbonium fragment on the adjacent nucleophilic centres.

The complex reaction involving unsaturated ketones such as methyl vinyl ketone gives rise to diketones [89]:



(44)

IV. APPLICATIONS OF THE SCHMIDT REACTION

The Schmidt reaction with ketones has come to be widely used as a convenient method for the synthesis of *N*-substituted amides with different structures, tetrazoles, and certain other compounds. Compared with other methods, it has the advantage of simplicity, ready availability of the reactants, and mild reaction conditions. The Schmidt reaction may be catalysed by protic and aprotic acids; sulphuric acid is normally employed for this purpose [11,36,90]. In many cases satisfactory results have been obtained using trichloroacetic acid [51,90] and particularly polyphosphoric acid [91,92].

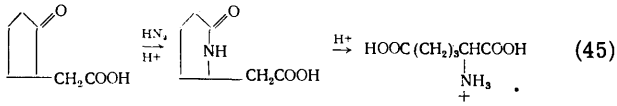
Solutions of hydrazoic acid required for the reaction are prepared beforehand or sodium azide is added directly to the reaction mixture. The use of hydrazoic acid *in situ* makes it possible to avoid direct contact with this explosive and poisonous compound.

Ketones of different structures, ranging from the simplest compounds to alkaloids [93], readily enter into the Schmidt reaction. The few failures reported in the literature can be accounted for by an unsuitable choice of reaction conditions.

The reaction of the carbonyl group of ketones with hydrazoic acid takes place selectively and does not involve functional groups such as the carboxy-, [94] ester [95], nitrile [40], and certain other groups.

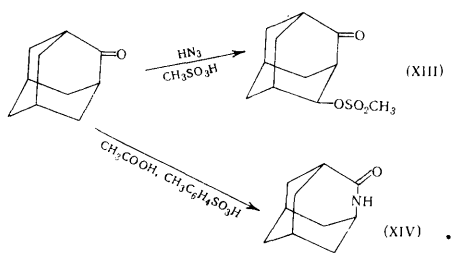
Aliphatic ketones react most readily. The reaction is frequently employed to determine the structure of the ketone or to synthesise the corresponding amide. In some cases amines containing other functional groups are obtained by this procedure. Thus α- and β-aminoacids are formed from acetoacetic or laevulinic acid esters.

The reaction with acyclic ketones takes place with ring expansion and leads to the formation of lactams [39]. Cyclic ketones containing carboxy- or ester groups are converted into lactams, which are hydrolysed under the reaction conditions to dicarboxylic acids [94,95]:



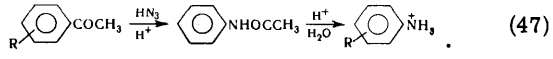
(45)

Depending on the reaction conditions, 4-methylsulphoxyadamantone (XIII) or the corresponding lactam (XIV) are formed from adamantone [96,97]



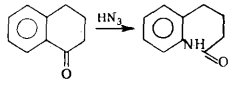
(46)

Alkyl aryl ketones have been investigated in the Schmidt reaction more than other carbonyl compounds. It has been shown that the reaction of substituted acetophenones with hydrazoic acid gives acetanilides in high yields [11,95,98]. This reaction is a convenient method for the preparation of various aromatic amines:



(47)

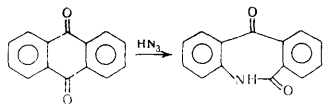
Cyclic alkyl aryl ketones such as tetralone [78] and benzosuberone [77] are converted into lactams under analogous conditions:



(48)

Compared with alkyl aryl ketones and aliphatic ketones, benzophenones are less reactive. However, when sulphuric acid is employed as a catalyst, satisfactory results are obtained[35,45]. Substituted benzophenones are of considerable interest, since the study of these ketones yields valuable information about the migration ratios in the Schmidt reaction.

Aromatic diketones behave somewhat differently in the Schmidt reaction. A complex mixture of products is obtained from benzil[82] and phenanthrenequinone[99] is converted into phenanthridone. Only one carbonyl group in anthraquinone and its amino-derivatives reacts[100]:



(49)

Ketones containing heteroatoms (nitrogen and sulphur) enter into the Schmidt reaction with formation of normal rearrangement products. Thus it has been shown that various carbonyl derivatives of thiophen are converted under the influence of hydrazoic acid in the presence of polyphosphoric acid into the corresponding amides in high yields[92,101]. A similar behaviour has been observed also for other heterocyclic ketones[102-104]. Ketones with a more complex structure, for example certain triterpenoids, give a mixture of amides and tetrazoles under the conditions of the Schmidt reaction[105].

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Mechanochemistry of Inorganic Solids

V.V.Boldyrev and E.G.Avvakumov

The chemical consequences of the mechanical treatment of inorganic solids has recently become the subject of detailed studies arising from increasing mechanical loading and the development of a highly effective technology of size reduction. The present review of published data examines the influence of mechanical treatment on the structural and thermodynamic properties of materials, the reactivities of substances, and the rates of physicochemical and chemical processes involving substances subjected to mechanical treatment. The possible mechanisms and characteristic features of mechanochemical processes are discussed, and routes to their practical utilisation are indicated. The bibliography contains 145 references.

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I. INTRODUCTION

In the search for new methods of carrying out processes in chemical technology and the development of methods for the directed control of the reactivity of solids, the study of processes taking place during the mechanical treatment of a substance has become extremely important. The mechanical treatment of solids (either beforehand or at the moment when the reaction is carried out), together with the use of heat, light, ionising radiation, electric fields, etc., provides one method for the physical stimulation of chemical processes, the possibilities of which have recently been extended considerably in connection with the development of highly effective techniques of size reduction.

Mechanochemical processes play a unique role in the chemistry of solids. Chemical reactions involving solids take place chiefly on a surface, and the state of the surface plays an important role in these processes. The action of heat on a solid leads to the excitation of all sites in the crystal lattice, whereas by mechanical treatment it is possible to bring only part of it into the excited state. There is another difference between the processes which take place on heating and on mechanical treatment. In thermal decomposition there is a slow increase in temperature, whereas on mechanical treatment there is a rapid pulse-wise increase in temperature at the points of contact between the friction solids, followed by rapid cooling. A consequence of this may be that in contrast to thermal decomposition, secondary processes may not be able to take place during mechanical treatment, and the primary products formed in the initial stages of the process are quenched. This may be one of the reasons for the specific features of the chemistry of mechanochemical reactions.

A number of reviews and monographs on the mechanochemistry of macromolecular organic substances have recently been published in the Soviet and other literature[1-7]. The aim of the present work is to review the mechanochemistry of inorganic solids. We shall therefore not deal here with problems of mechanochemical treatment of organic materials, and we shall not concern ourselves with special problems, such as the mechanochemical corrosion of metals, the study of which has recently undergone extremely intensive development[8-12].

In the examination of mechanochemical phenomena it is necessary to deal with two aspects, which are difficult to separate from one another. The first is the production of new physicochemical properties by the production of finely dispersed particles with increased energy. The second concerns the chemical changes taking place during the treatment of a substance under the influence of the physical processes taking place.

Since the problems of the state of finely dispersed particles have been fairly fully reviewed[13], most attention in the present review is paid to the second aspect, and also to the discussion of the specific features and nature of mechanochemical reactions.

II. PRODUCTION OF NEW PHYSICOCHEMICAL PROPERTIES AS A RESULT OF DISPERSION

1. Change in Free Energy, Solubility, and Thermal Stability

The process of size reduction can be regarded not only as a process of increasing surface area, but also as a process of increasing free energy (chiefly surface free energy). In this sense it can be said that size reduction is also a chemical process, since a change in free energy leads to a displacement of chemical and phase equilibria. The absence of excess free energy in a solid leads to the production of thermodynamically unstable states. A higher concentration of excess free energy corresponds to a higher content of excess internal energy ΔH and an excess entropy ΔS.

When the entropy change is small (the crystalline state is preserved), the change in free energy can be estimated from the change in excess enthalpy by calorimetric methods[14]. According to published work[15,16], the increase in enthalpy, for example, for oxides on going from the single crystal to the finely divided state is 1–3 kcal mole^{-1}. If the entropy change cannot be neglected, the excess free energy can be measured by measuring the equilibrium position of a chemical reaction in which the activated substance reacts with another substance of known activity.

From the relationship

$$\Delta G = -RT \ln \frac{k_2}{k_1} \quad (1)$$

where ΔG is the change in free energy and k_1 and k_2 the rate constants of the forward and back reactions respectively, it can be seen, for example, that a change in ΔG from 0 to 20 kcal mole^{-1} leads to a change in the ratio of k_2 to k_1 from 1 to 1×10^{15}. An example is provided by the reaction [18]

$$Ni + 4CO \rightleftarrows Ni(CO)_4. \quad (2)$$

The equilibrium position of the reaction is displaced to the right with increase in the surface area of the nickel, for example on going from nickel foil to nickel dust. The change in free energy is 1.38 kcal mole^{-1}; the ratio k_2/k_1 changes accordingly by one order of magnitude.

The free energy of finely dispersed particles can be estimated approximately by means of Thomson's equation

$$\Delta G = \frac{2\sigma V}{r}, \quad (3)$$

where σ is the surface tension, r the particle radius, and V the molar volume. Eqn. (3) is approximate, if only because the value of σ must also change when the particle dimensions become very small.

The fine particles exhibiting increased values of the free energy differ from large particles in other properties. In particular, if the particles are sufficiently small, their dissolution may produce concentrations exceeding those corresponding to the usual equilibrium solubility of the substance. Ostwald, and later Freundlich, obtained equations giving the dependence of the solubility on the dimensions of the particles [19]:

$$\ln \frac{C_r}{C^*} = \frac{2\sigma M}{RT\rho r}, \quad (4)$$

where C_r is the solubility of the particles with radius, r, C^* the equilibrium solubility, ρ the density of the solid, and M the molecular weight.

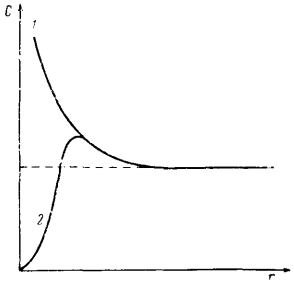

Figure 1. Dependence of solubility on particle size.
1) Freundlich's equation, *2*) Knapp's equation.

The Ostwald–Freundlich equation contains the same assumptions as were made in the derivation of Thomson's equation. For example, it is assumed that the density of the solid and the surface energy are independent of the particle dimensions.

The solubility of finely dispersed particles was examined from another viewpoint by Knapp [20]. He assumed that the particles carry a small surface electric charge, so that the total surface energy is the sum of the surface and electrical energies. On the basis of these assumptions he derived for isolated charged particles the equation

$$C_r = C^* \exp\left(\frac{a}{r} - \frac{b}{r^4}\right), \text{ where } a = \frac{2\sigma M}{RT\rho}, \; b = \frac{QM}{8\pi RT\varepsilon\rho}, \quad (5)$$

Q is the electrical charge of the particle, and ϵ the dielectric constant of the solid. Eqn. (5) gives the curve shown in Fig. 1. The experimental data obtained by Dundon and Mack [21,22] can be regarded as confirming Knapp's conclusions.

A large amount of work has shown that the increase in the surface area of solid particles produced during size reduction leads to an increase in the rates of solid-phase reactions, in particular decomposition [23]. In a number of instances the rates of topochemical reactions pass through a maximum with decrease in the particle dimensions. The reason for this dependence is that with change in the degree of dispersion, the ratio between the rate of formation of the nuclei of the new phase and the rate of their growth changes in such a way that the rate of the process is determined in some instances by nucleous formation, and in other instances by the growth of nuclei [24-26].

2. Kinetics of Size Reduction and the Dissolution of a Finely Divided Substance

Irrespective of the type of apparatus used for size reduction (with the condition that the apparatus is efficient and operates for a sufficiently long time), the change in the particle dimensions on size reduction takes place in three stages [27-30]. The first stage is characterised by a progressive decrease in the particle dimensions with time; the second by the start of aggregation of the particles; and the third by the establishment of equilibrium, in which the particle dimensions remain unchanged with time. The specific surface changes analogously. A characteristic picture of the change in the specific surface and particle dimensions on size reduction is given in Fig. 2.

For the description of the dependence of the particle dimensions on the duration of the size reduction, Schneider [31] proposed the equation

$$\frac{dr}{dt} = -k_0 e^{-\frac{U_B}{U_M}}(r - r_g) + k_r e^{-\frac{U_a}{f\frac{\sigma}{r} + \frac{E}{2}\left(\frac{A}{B + r^n}\right)^2 + U_M}}, \quad (6)$$

where r represents the particle size, r_g the minimal particle size, k_0 the rate constant for the formation of fractures in the lattice, k_r the recrystallisation rate constant, U_B the mean specific energy of fracture, U_M the specific mechanical load, U_a the activation energy of the recrystallisation process, E the modulus of elasticity, and A, B, f, and n constants.

The first term in the right hand side of Eqn. (6) describes the breakdown of the substance, whereas the second term describes the recrystallisation. The quantities appearing in the equation depend on the nature of the substance undergoing size reduction, and in particular on the type of chemical bonding. For ionic compounds the activation energy of recrystallisation is small, whereas for covalent compounds it is much larger (greater energetic interference is required to restore broken

valency bonds). As a consequence, the $dr/dt = \varphi(t)$ curves for ionic compounds pass through a minimum; for covalent compounds the minimum is poorly defined, or completely absent; in the last instance the particle size decreases smoothly with time until the equilibrium value is reached.

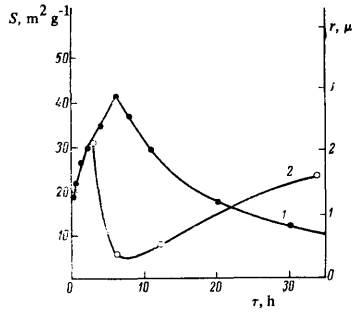

Figure 2. Dependence of specific surface and particle size on duration of size reduction: *1*) specific surface; *2*) particle size.

The specific surface (and the particle size) are influenced to a significant extent by the medium in which the size reduction is carried out. In a study of the mechanical properties of inorganic crystals (galena, calcite, and graphite), Rebinder [32] established that the strength of these crystals is greatly reduced in the presence of surface-active substances. He showed that the changes in the mechanical properties of solids under the influence of surface-active substances results from a decrease in the surface free energy and hence a decrease in the work required to increase the surface area. The decrease in hardness with change in the concentration of surface-active substance takes place in parallel with a change in adsorbability, and is described by an equation analogous to Langmuir's equation

$$\Delta B = \Delta B_\infty \frac{C}{C+\alpha}, \qquad (7)$$

where ΔB is the decrease in hardness, C the concentration of surface-active substance, ΔB_∞ the total decrease in hardness on complete saturation of the absorption layer, and α a constant.

The phenomenon of adsorption decrease in strength under the influence of surface-active substances (the Rebinder effect) provides a basis for the development of methods for controlling the rate of size reduction of solids [33,34]. Despite the fact that with increase in the duration of dispersion the specific surface increases only as far as a certain limit, the breakdown of the crystal lattice continues until the substance is completely converted into the amorphous state [29,30]. Because of the presence of the amorphous state, the solubility increases on size reduction, and the maximal attainable solubility may exceed the normal solubility. Khodakov and Plutsis established that the solubility of quartz in water, after size reduction on a vibro-mill, is given by the equation

$$C = C_\infty(1 - e^{-k\tau}), \qquad (8)$$

where C_∞ is the maximal solubility, τ the duration of size reduction, and k a constant. Eqn. (8) is also applicable to other substances [13,14].

An increase in solubility under the influence of mechanical treatment was also observed for iron oxide [35], copper oxide [16], sodium chloride [16], calcium carbonate [35,36], quartz [29,37,38], bauxite [30], monazite [6], alumina [39], tin(IV) oxide [40], chromite [41], etc.

3. Phase Transformations and Behaviour of Solid Solutions on Size Reduction

Very fine particles with an increased energy content are responsible for the production of metastable states and phases on size reduction. An example is provided by data [42] which show that decrease in particle size is accompanied by an increase in the temperature and enthalpy of solid-phase transformations in quartz, potassium sulphate, and potassium nitrate.

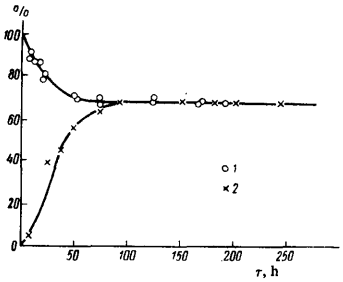

Figure 3. Equilibrium between the two crystalline phases of calcium carbonate under the influence of mechanical treatment [43]. *1*) Aragonite, *2*) calcite.

Under the influence of prolonged size reduction, an equilibrium is established between different modifications of a substance. Thus for example, equilibrium between calcite and aragonite is established after grinding for 80 h in a vibro-mill (Fig. 3) [43]. The high-temperature forms of the substances are also detected during the grinding of zinc sulphide [44], cadmium sulphide and selenide [45,46], barium chromate [47], silicon carbide [47], titanium dioxide [47], silver iodide [48], calcium carbide [49], lead dioxide [50], sulphur [51], selenium [52], quartz [53], nephelite [53], etc.

The establishment of thermodynamic equilibrium between solid phases depends on the rate of diffusion of the components of the mixtures. Since the size reduction of crystals leads to a sharp increase in the number of vacant sites in the lattice [54] and hence to an increase in diffusion and ionic conductivity in ionic crystals, the rate of attainment of thermodynamic equilibrium increases under the influence of size reduction.

The size reduction of a mixture of isomorphous components facilitates solid solution formation. It has been found [55,56] that solid solutions of potassium chloride and bromide can be obtained by grinding them in a mill or by repeated application of pressure to 13 000 atm. If a mixture of two substances is a solid solution of components which mix with difficulty, for example NaCl–TlCl (0.6 mole %) or KCl–AgCl (0.6 mole %), grinding of the solid solution leads to its partial breakdown [57].

III. CHEMICAL REACTIONS DURING THE MECHANICAL TREATMENT OF A SUBSTANCE

1. Decomposition and Preparation of Substances

The possibility of decomposing inorganic substances by grinding was established at an early date. As early as last century it was shown that grinding leads to the decomposition of many solid salts of silver and mercury[58,59]. The mechanochemical decomposition of a large number of inorganic compounds: carbonates, oxalates, nitrates, halates, complexes, etc. has now been studied.

Decomposition to the following extents after grinding for 20 h in a vibro-mill has been reported[60,61]: magnesium carbonate 28.9%, calcium carbonate 13.9%, strontium carbonate 10.8%, barium carbonate 8.4%, sodium carbonate 0.22%, and potassium carbonate 0.16%. Decomposition gives the oxides and oxygen.

Direct mass-spectrometric measurements[62] showed that the average number of monolayers decomposed in the size reduction of crystals of lead, magnesium, and calcium carbonates is 2, 0.37, and 0.09 respectively. The mechanochemical decomposition of calcium carbonate has been studied in detail[43]. The equilibrium thermal dissociation pressure, enthalpy of dissolution, particle size, and specific surface after mechanical activation were determined. The equilibrium pressure of carbon dioxide was used to calculate the values of ΔG, ΔH, and ΔS. Mechanical activation decreases the values of these quantities for thermal decomposition at 625°C: ΔG from 8.1 kcal mole^{-1} to 6.2 kcal mole^{-1}, ΔH from 33.2 kcal mole^{-1} to 14.8 kcal mole^{-1}, and ΔS from 28.0 e.u. to 9.6 e.u.

The decomposition of iron, zinc, and manganese carbonates is analogous. Peters[6] showed that different products may be obtained, depending on the conditions of mechanical treatment. The decomposition of iron carbonate (siderite) in air gives the oxide Fe_2O_3; in the presence of moisture the hydroxide $Fe(OH)_3$ is obtained. When the carbonates are subjected to size reduction in a vacuum, the quantity of carbon dioxide liberated is greater by an order of magnitude than that for decomposition in air. In the size reduction of sulphides (for example cinnabar[63]), decomposition to the metal and sulphur may take place.

A large amount of work has been done on the study of the effect of mechanical action on the decomposition of explosives. The thermal theory of the initiation of explosions by mechanical action has been intensively developed[64]. Criteria by means of which the mechanical sensitivity of explosives might be characterised have not been established, however.

To investigate the characteristic features of mechanochemical decomposition, the properties of the product of the mechanochemical decomposition of silver oxalate were compared with the properties of the product of its thermal decomposition[65]. The results indicated that the activity of "mechanochemical" silver is much less than that of silver obtained by thermal decomposition, but much greater than the activity of photochemical silver.

The mechanochemical decomposition of alkali metal, alkaline earth metal, and rare earth metal nitrates has been studied[66,67]. The degree of decomposition of the alkali metal nitrates was determined from the yield of nitrate, and that of the alkaline earth metal nitrates and anhydrous lanthanum nitrate from the yield of metal oxide. The decomposition curves have the same form as the specific surface curves, that is the degree of decomposition passes through a maximum, after which an equilibrium state is established (Fig. 4). The existence of this correlation may indicate that the mechanochemical reactions are localised on the surface of the substance subjected to size reduction. The decomposition curves before the maximum are described satisfactorily by the equation

$$\alpha = k\tau^n \qquad (9)$$

where α is the degree of decomposition, τ the time, and k and n constants[68]. For the substances studied, $n = 3$.

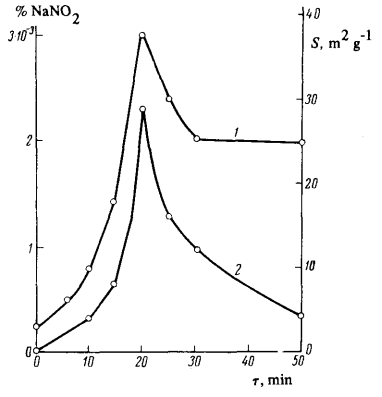

Figure 4. Dependence of the specific surface and yield of the product of the mechanochemical decomposition of nitrate on the duration of size reduction. *1*) Specific surface, *2*) $NaNO_2$ concentration.

With increase in the mechanical energy supplied, the degree of decomposition of the substances increases but the form of the curve is preserved. This can be seen from Fig. 5, which shows curves giving the dependence of the mechanical decomposition of sodium nitrate on the acceleration developed in a centrifugal planetary mill[67]. It follows from published data[66], reproduced in Fig. 6, that in a series of nitrates of the same type, the degree of decomposition increases with decrease in the crystal lattice energy. An analogous dependence is observed for the decomposition of substances under the influence of an explosion[69,70]. The similarity between the decomposition of substances on grinding and decomposition under the influence of an explosion is also shown in the fact that identical decomposition products are formed, for example in the decomposition of copper compounds[69,71].

The rate of mechanochemical decomposition may change in the presence of substances which exhibit redox properties or which act as catalysts. The decomposition of minerals and salts takes place particularly readily in the presence of ammonium salts or their mixtures with one another[72]. The rate of decomposition of substances can be altered by introducing catalysts, such as transition metal oxides. It has been shown[73] that the rates of decomposition of sodium nitrate in the presence of Ni, Fe, Zn, Cu, and Mn oxides show a correlation with the work function of an electron from the oxide.

When a mixture of substances is ground, synthetic and exchange reactions take place between them. The sulphides of Hg, Ag, Mg, Cd, Zn, Sn, Pb, Sb, and Bi are formed in yields of 25–100% when the metals are ground with sulphur, carbides are obtained by grinding with graphite, phosphides by grinding with phosphorus, iodides with iodine, etc.[69,72,74].

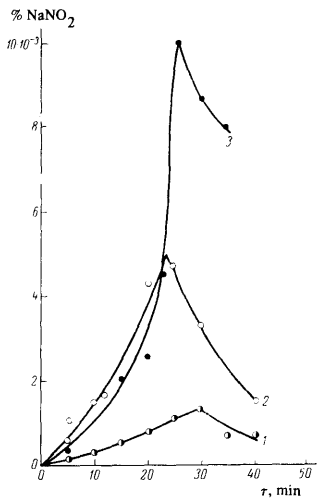

Figure 5. Influence of mechanical load on the degree of mechanochemical decomposition of sodium nitrate. Acceleration:
1) 20g, *2*) 40g, *3*) 60g.

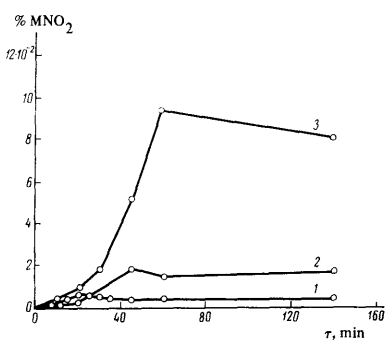

Figure 6. Mechanochemical decomposition of alkali metal nitrates.
1) $NaNO_3$, *2*) KNO_3, *3*) $CsNO_3$.

Oxides are formed when metals are ground in the presence of atmospheric oxygen[4]. The rate of oxidation passes through a maximum, depending on the duration of grinding, and before the maximum it is described by the equation

$$\ln v = k\tau + c \qquad (10)$$

where v is the rate of oxidation, and k and c constants.

Metal carbonyls, in particular Ni, Fe, and Zn carbonyls[75-77], can be obtained by a mechanochemical method. Detailed study of the carbonylation of nickel has established that mechanochemical treatment lowers the activation energy of the formation of nickel carbonyl from 10.2 kcal mole^{-1} to 2.1 kcal mole^{-1} [75]. The rate of formation of nickel carbonyl may be altered by the presence of additives of different types. It has been shown[76,77] that substances such as O_2, $KClO_3$, $K_2Cr_2O_7$, $KMnO_4$, KI_2O_3, Na, Ca, and I_2 decrease the reaction rate, whereas the addition of sulphur and compounds containing sulphur has an activating influence on the formation of carbonyls. It is considered that the catalytic activity of these compounds is due to the formation of the intermediate compound γ-NiS.

Mechanochemical treatment can be used to prepare silicates from silicon dioxide and alkali and alkaline earth metal oxides or carbonates, and to prepare molybdates and tungstates from carbonates and oxides[6]. It has also been possible to carry out preparations which could not be carried out by other methods. Mechanochemical processes have been used to prepare catalysts with high selectivity[78,79], spinels[80], dyes[81], metallates[82], organometallic compounds[83], etc.

A large number of exchange reactions take place on grinding, and these have been used to develop simple methods of qualitative chemical analysis[59,72,84,85].

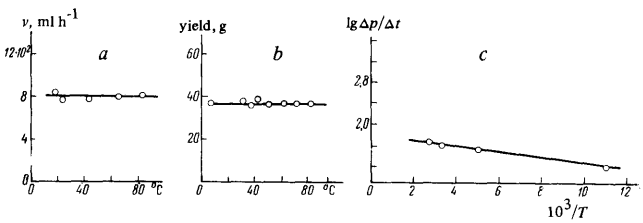

Figure 7. Temperature dependence of the rate of mechanochemical reactions[86-88].
a) $SiC + 2H_2O \rightarrow CH_4 + SiO_2$, *b*) $Sn + 2C_6H_5CH_2Cl \rightarrow (C_6H_5CH_2)_2SnCl_2$, *c*) $2Fe + O_2 \rightarrow Fe_2O_3$.

2. Influence of Temperature on Mechanochemical Reactions

One of the features indicating the specific nature of mechanochemical reactions is the fact that they are independent of temperature. Published data[86-88] on the influence of temperature on the rate of mechanochemical reactions are given in Fig. 7. The reaction rates remain almost unchanged (Fig. 7). Analogous results were obtained in a study of the decomposition of nitrates at room temperature and at the temperature of liquid nitrogen[66].

3. Formation of Free Radicals and Reactions Taking Place on Freshly-formed Surfaces

Measurements made on powders show that in diamagnetic substances after size reduction, paramagnetic centres resulting from the production of free radicals appear in the surface layers to a depth of 20–30 μ.

The regular features of the formation of radicals in the size reduction of quartz and their reaction stability at elevated temperatures have been studied[89-93]. Concentrations of unpaired electrons of the order of 10^{14} to 10^{15} g^{-1} were obtained. With decrease in the size of the particles their concentration increases. According to some authors[94], the paramagnetic centres in quartz are stable at 120°; their concentration decreases linearly in the range 120–360°. According to other data[92], the free radicals produced in quartz are stable as far as 350–400°, so that they can be preserved for a long time at room temperature.

The infrared spectrum of quartz after size reduction[95] showed a peak at 950 cm^{-1} due to the siloxane group SiOH. The production of the peroxo group ≡Si:O:O as a result of the mechanical treatment of quartz has been established[96].

It has been shown[97] that on the surface formed by the size reduction of graphite crystals, the carbon atoms are in two different electronic states—atoms in a bivalent singlet state and atoms forming over-stressed quasi-acetylenic bonds; free radicals containing carbon atoms with broken π- and σ-bonds are also present.

The EPR spectrum of zinc oxide subjected to mechanical treatment has been studied. The spectrum of the original zinc oxide showed two weak signals with $g = 2.006$ and $g = 1.956$, of approximately equal intensity. After the specimen had been ground in a mortar, the EPR spectrum, in place of the singlet with $g = 2.006$, showed a strong unsymmetrical triplet superimposed on a weaker spectrum, from which two components could be seen; with decrease in temperature to −196° these components increased by a factor of 4, whereas the amplitude of the triplet remained almost unchanged. The singlet with $g = 1.956$ decreased by a factor of several times after the substances had been ground. The EPR spectrum produced on grinding remains unchanged when the specimen is exposed to air, on evacuation of 10^{-3} mmHg, on treatment with solvents, or when iodine and quinone are adsorbed on its surface, but it gradually disappears when the specimen is heated above 100° in a vacuum or in air.

The EPR spectra of silicon, germanium, silicon carbides, diamond, the oxides of magnesium, calcium, strontium, and zinc, calcium and zinc sulphides, quartz, and α-alumina have been studied[88,90]. It has been stated[93] that the spectra obtained after mechanical treatment show a similarity to the spectra obtained after the irradiation of substances with fast neutrons. This is observed particularly clearly for magnesium and silicon oxides, for which both mechanical treatment and irradiation with neutrons lead to the formation of an F-centre with identical g-factor for the single signal.

As a consequence of the formation of active centres on the surface, reactions which do not take place under ordinary conditions become possible. An increase in pH and the bonding of atmospheric nitrogen as nitrate and ammonia has been observed on size reduction of sodium chloride. The change in the concentration of hydroxide ions was found to be proportional to the square of the surface area. The authors cited consider that the binding of nitrogen as the compounds on sodium chloride particles produced by the evaporation of sea water is an extremely important source for the accumulation of nitrogen compounds in the atmosphere.

The influence of the mechanical breakdown of crystals (NaCl and $BaSO_4$) on the polymerisation of vinyl monomers has been studied[100]. It has been shown that the initiation of the formation of polymers is brought about by the electron emission arising on breakdown of the crystals (mechano-electrons) and not by static defects in the solid phase (vacancies, colour centres, etc.), obtained by preliminary irradiation of the salts.

IV. MECHANISM OF MECHANOCHEMICAL REACTIONS

1. Physical Phenomena on Grinding

In early work on the mechanochemical reactions of solids[72,101], the chief role was assigned to particles of moisture adsorbed on the surface. It was assumed that there is no fundamental difference between reactions taking place in concentrated solutions and reactions taking place on grinding. It was established[102], however, that there is no relationship between the rate of reaction on grinding and the solubility of a salt. Moreover, it was established that in a number of instances, water decreases the reaction rate. It was found that a more important role in mechanochemical reactions is played by physical processes taking place on contact between solids in friction. The following phenomena are related to these processes.

Liberation of heat. When solids slide together, the greater part of the work done against the forces of friction is liberated in the form of heat. At locally restricted points on the surface, the temperature reaches an extremely high value. Bowden and Tabor[103] showed theoretically and experimentally that in sliding friction the temperature at the points of contact increases as far as the melting point, but never rises above it. For refractory substances, an instantaneous local increase in temperature to 1000°C may be achieved in the surface layer. The main bulk of the substance at this moment remains cold. The duration of existence of these temperature spikes on an area of 10^{-3}–10^{-5} cm is of the order of 10^{-4} s.

Production of high pressures. At the points of contact of friction solids, the production of a high temperature is accompanied by a simultaneous short-lived increase in pressure. The magnitude of this pressure has been estimated[104]. A series of substances for which the pressures (bar) of the phase changes were known were taken: PbO 5500, MnF_2 9500, Sb_2O_3 10 800, SiO_2 13 500, BeF_2 17 500, B_2O_3 18 500, and $BaAsO_4$ 30 000. The substances were ground in a mill, after which the ground products, for all the above substances except $BaAsO_4$, were found to contain the modifications existing at high pressures. On the basis of these data it was concluded that on contact between the solids in the mill, pressures of up to 15 000 bar were developed.

Production of electric charges. On friction between solids, electric charges are produced. The reasons for the production of electric charges on surfaces are varied. According to one view[105], solid dielectrics, because of the presence of structural defects, carry on their surface a charge which is compensated by ions adsorbed from the air. On friction, the compensation of the intrinsic charges is destroyed, and electrification results.

It has been shown[106] that the charges produced on contact between semiconductors and metals are linearly dependent on the difference in the work functions of an electron from the solids in contact.

When the surface of a crystal carries a charge, a space charge with sign opposite to the sign of the charge on the surface is produced in the volume of the crystal in order to preserve its electrical neutrality; this space charge undergoes oscillations (like the oscillation of the charge between the plates of condensers[107]). In large crystals the amplitude of the oscillations of the space charge is small, and the magnitude of the varying potential difference produced on breakdown of the crystal is correspondingly small. As the size of the crystal decreases, the potential difference increases, but for very small crystal dimensions it decreases again. The potential produced on the surface of ionic crystals under the influence of shock or deformation shows a correlation with the plasticity of the crystal[108]. The softer the crystal, the higher the potential, and vice versa.

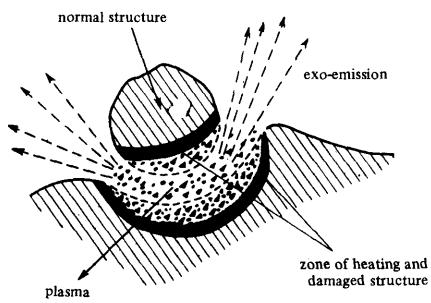

Figure 8. "Magma-plasma" model of mechanochemical processes[4].

Exo-emission and mechano-emission of electrons. In solids at the moment of mechanical treatment and afterwards, mechano-emission and exo-emission of electrons takes place. The electrons of the exo-emission, which is quenched extremely slowly after mechanical treatment, have an energy not greater than 1 eV, [109] whereas the mechano-emission electrons (mechano-electrons) have energies of tens of keV. [110] Exo-electronic emission results from heating, irradiation, chemosorption, etc., that is it is similar to thermal emission with its over-the-barrier removal of electrons. The mechano-electrons obtain their high energy by acceleration in the field of a "micro-condenser", the plates of which are the separated surfaces of the fracture. The electrons tunnel through the barrier, as a consequence of the high electric field.

Triboluminescence. When solids are subjected to size reduction and shock, extremely intense luminescence is produced. Most workers consider that the triboluminescence is associated with electric charges produced between the broken particles[111]. In triboluminescence accompanying the breakdown of ionic crystals in air, the nitrogen spectrum observed is the same as that for an electric discharge.

With allowance for the physical phenomena associated with size reduction, Thiessen and coworkers[4] put forward a "magma-plasma" model of mechanochemical processes (Fig. 8). According to this model, the energy liberated on shock or grinding, as a consequence of the low thermal conductivity of solids, leads not only to a local increase in temperature and sublimation of the substance, but also to the production of a state of the substance in which it exists in the form of ions and electrons (plasma). It was noted above that in the decomposition of substances under the influence of an explosion and on grinding, identical products are obtained. On this basis it may be stated that when a substance is ground, characteristic "micro-explosions" take place on contact between the solids in friction. These results also provide evidence in support of the "magma-plasma" model.

The production of the above phenomena on mechanical treatment brings mechanochemical reactions closer to plasma reactions, and if the treatment is carried out in aqueous medium, conditions are created for hydrothermal reactions.

2. Comparison with Reactions Taking Place Under the Influence of Heat, Light, and Radiation. Mechanochemical Equilibrium

It can be seen from the foregoing that mechanochemical reactions show almost no temperature dependence, whereas the latter is a characteristic feature of reactions taking place under the influence of heat. Another characteristic feature of mechanochemical reactions is that the reactions may take place by a thermodynamically unfavourable route. An example is provided by the decomposition of the alkali metal bromates, which can take place by two reactions:

$$MBrO_3 \rightarrow MBr + {}^3/_2O_2 \ . \qquad (11)$$

$$MBrO_3 \rightarrow {}^1/_2M_2O + {}^1/_2Br_2 + {}^5/_4O_2 \ . \qquad (12)$$

The free energy (T = 298°K) for reaction (11) is negative, and that for reaction (12) is positive. Mechanochemical decomposition, however, takes place almost entirely according to Eqn. (12)[112]. Data for other reactions taking place by a thermodynamically unfavourable route have been published[113].

The tribochemical decomposition of a number of inorganic substances has been studied[64], and a correspondence between the start of the thermal decomposition and the ability to undergo mechanochemical decomposition was not observed. Thus for example, the temperature of the start of decomposition of ammonium chromate is 110°, but it does not decompose on grinding, whereas mercury(I) chromate, for which the temperature of the start of thermal decomposition is 500°, decomposes readily on grinding. A large number of studies[114,115] have shown that the mechanochemical splitting of molecules gives products which have nothing in common with the products of thermal decomposition, and reactions which take place in the opposite direction on heating are possible[6].

In a study of the reaction of copper with water under the influence of mechanochemical activation, it was found that after grinding for 5–6 d, more than 2% of metallic copper reacts with water with the liberation of hydrogen[12]. The equilibrium constants for the reaction of copper with water in the range 298–3000°K are given in Table 1. Calculation shows that even at 3000°K the partial pressure of hydrogen should not exceed 10^{-2} mmHg. The experimental data show that the pressure exceeds the calculated

value by a factor of 1000. It was concluded that the local-heating theory cannot explain the displacement of hydrogen by copper.

Peters[6] showed that the reactions taking place on mechanical treatment are reversible. For example, treatment of zinc oxide in the presence of carbon dioxide leads to the formation of zinc carbonate, whereas dissociation of zinc carbonate takes place on treatment in a vacuum. In recent years, many systems in which mechanochemical reactions take place in both directions have been detected[116]. If the rates of the forward and reverse reactions on mechanical treatment are equal, there is no overall macroscopic change in the system.

Table 1. Thermodynamic calculation of equilibrium constants[12].

Reaction	ΔG, kcal mole^{-1}	k_r, °K			
		298°	1000°	2000°	3000°
$Cu + H_2O_{gas} \rightarrow CuO + H_2$	+24.2	10^{-18}	10^{-17}	10^{-5}	10^{-4}
$2Cu + H_2O_{gas} \rightarrow Cu_2O + H_2$	+19.6	10^{-15}	10^{-5}	10^{-5}	10^{-3}

For purely thermal action, we speak of chemical equilibrium. In contrast to chemical equilibrium, the steady state produced on mechanical treatment is described as mechanochemical equilibrium.

Quantitative data on mechanochemical equilibrium in the system $CdC + CO_2 \rightleftharpoons CdCO_3$ have been obtained[116]. The dependence of the reaction rate on the carbon dioxide pressure and the composition of the solid phase are shown in Fig. 9. A positive value of the ordinate denotes the forward reaction, and a negative value the back reaction. For different compositions of the solid phase, the reaction rate becomes equal to zero at different CO_2 pressures. This steady state can be reached from two directions. Fig. 9 shows that mechanochemical equilibrium differs from chemical equilibrium. The position of chemical equilibrium does not depend on the concentration of carbonate in the solid phase. According to Gibbs' phase rule, in the carbonate system $MCO_3 + MO + CO_2$, each temperature corresponds to a definite CO_2 pressure. Thus the equilibrium pressure for the $CdCO_3 + CdO + CO_2$ system is $p_{CO_2} = 133 \times 10^{-6}$ mmHg at 298°K, whereas for the carbonate subjected to preliminary mechanical treatment $p_{CO_2} = 1.7$ mmHg at 298°K. It can be seen from Fig. 9 that on mechanical treatment the pressure corresponding to mechanochemical equilibrium depends markedly on the composition of the material undergoing size reduction. With change in the concentration of $CdCO_3$ from 50 mole % to 90 mole % the equilibrium pressure of CO_2 increases by approximately two orders of magnitude. For pure cadmium carbonate at mechanochemical equilibrium the CO_2 pressure is $p_{CO_2} =$ 660 mmHg at 298°K.

The next difference between mechanochemical and chemical equilibrium is that its maintenance requires the irreversible introduction of mechanical energy into the system. In this respect, mechanochemical processes are similar to photochemical and radiochemical processes.

As shown above, radical formation is possible when inorganic solids are ground. The first stage in a mechanochemical reaction may therefore be bond rupture and the formation of free radicals, the second stage being the reaction of the free radicals. Thus in some instances the overall picture of mechanochemical transformations shows features in common with radiochemical reactions[117].

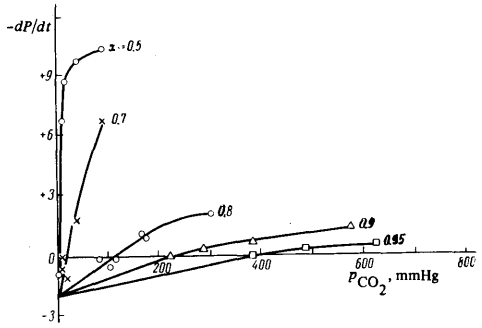

Figure 9. Dependence of the rate of reaction in the $CdO + CO_2 \rightarrow CdCO_3$ system on the pressure of CO_2 and the composition of the solid phase[116] (x is the mole fraction of $CdCO_3$).

The mechanochemical decomposition of alkali and alkaline earth metal nitrates, and the decomposition of sodium nitrate in the presence of heterophase (metal oxides) and homophase (added by cocrystallisation) additives have been studied[66] in order to compare the results with thermal, radiochemical, and photochemical decomposition. The results showed that, as in radiation decomposition, a correlation is observed in mechanochemical decomposition between the degree of decomposition and the free volume. The correlation is less distinct, however, than that for radiation decomposition. A correlation between the degree of mechanochemical decomposition and the order of the thermal stabilities of these compounds is not observed, however. An analogous picture is observed when the action of homophase and heterophase additives is compared.

3. Characteristic Kinetic Features of Mechanochemical Reactions. The Role of Non-equilibrium States

Since the decomposition of molecules on mechanical treatment takes place chiefly in the surface layers and the layers next to the surface, the rate of the mechanochemical decomposition of molecules is determined in the initial stages of size reduction by the rate of increase in the surface area, which depends on the nature of the substance undergoing size reduction and also on the type of size-reducing apparatus. After the particle radius during size reduction has decreased to the thickness of the surface layer, a constant maximal rate of decomposition is established. As a consequence of the recrystallisation which takes place on size reduction, however, a decrease in the rate of mechanochemical decomposition may take place after the maximum rate has been reached. If during size reduction conditions are created for the reverse reaction (for example through the difficulty of removing reaction products from molecularly compact aggregates), a state of mechanochemical equilibrium is established.

To explain the nature of the process of bond rupture in mechanically stressed molecules, Zhurkov[118] suggested that under the influence of stress, the F-energy [dissociation energy? (Ed. of Translation)] of the bond Q decreases by an amount of energy ϵF, and the rate constant for bond rupture k increases according to the equation

$$k = k_0 \exp\left(-\frac{Q-\epsilon F}{RT}\right) \quad (13)$$

where k_0 is a constant, with order of magnitude close to that of the vibrational frequency ($\sim 10^{13}$ s^{-1}).

It was shown above that the rate of mechanochemical processes either is weakly dependent on temperature or is characterised by a negative temperature coefficient[119], so that Eqn. (13) is not applicable in all instances.

To explain the nature of mechanochemical processes, Butyagin[120] introduced the concept of non-equilibrium states of bonds in molecules. This makes it possible to explain why small energies are sufficient to bring about mechanochemical decomposition (this differs from the "magma-plasma" model, according to which mechanochemical decomposition takes place as a consequence of the liberation of large amounts of energy on contact between colliding particles).

On mechanical treatment the energy of deformation of a bond is converted into thermal energy and redistributed between other bonds. This excess energy, the magnitude of which is much smaller than the bond strength, may be sufficient for the rupture of bonds present in a non-equilibrium state. On the basis of this assumption, Butyagin obtained an equation for the rate constant of the mechanochemical reaction, of the following form

$$k = A \exp\left(-\frac{E_M^*}{\Delta E_M}\right) \quad (14)$$

where A is a coefficient which takes account of the rate of redistribution of the mechanical energy in the system, E_M^* is the minimal mechanical energy required for bond rupture, and ΔE_M the average level of the excess energy.

It is assumed that on mechanical treatment of a substance, the rate of absorption of the mechanical energy supplied is to a first approximation proportional to the intensity of its introduction I, and the rate of relaxation of the stresses is proportional to the average level of the excess energy ΔE_M. In the steady state the rates of the two processes are equal, that is

$$\gamma I - k_r \Delta E_M = 0 \quad (15)$$

where γ is a dimensionless coefficient which takes account of the efficiency of absorption of the mechanical energy, and k_r the rate constant for the relaxation of the stresses. With allowance for Eqn. (15), Eqn. (14) becomes

$$k = A \exp\left(-\frac{k_r E_M^*}{\gamma I}\right). \quad (16)$$

If the dependence of the rate constant of a mechanochemical reaction on the quantity of mechanical energy introduced is determined, the values of A, E_M, and k_r can be calculated from Eqn. (16). Experimental data on the mechanochemical decomposition of polymethyl methacrylate and quartz, treated by means of Eqn. (16), give values of A 10^{-3}–10^{3}, $E_M^* \sim 10$–10^2 kcal, $\gamma \sim 1$–10^{-3}, and $k_r \sim 10^{-1}$–10^{-4} s^{-1}. It can be seen that E_M^* is much smaller than the bond energy Q, and A differs from k_0 by several orders of magnitude.

Analogous concepts were used by Bartenev and Razumovskaya[121] to develop the concept of the phonon breakdown of brittle solids. They consider that in the breakdown of solids it is necessary to examine not the thermal vibrations of the atoms but the propagation, interaction, and generation of phonons. The stages in the breakdown of a solid (the first is the formation of defects, and the second the growth of micro-cracks from these defects) can be regarded as independent processes only in the initial period. As the defects develop, the energy liberated on rupture leads to an increase in the density of phonons of definite frequencies (non-equilibrium phonons). This energy source influences both the development of the actual defect generating the phonons, and also the development of neighbouring defects.

There is thus a fundamental difference between the rupture of bonds in a solid and the rupture of bonds between isolated atoms in a molecule. The change to the phonon concept makes it possible, as the authors cited assert, to introduce for each structure a characteristic spectrum, which can be obtained experimentally, and also to use the achievement of the modern quantum theory of solids to develop a theory of breakdown processes.

V. PRACTICAL ASPECTS OF MECHANOCHEMISTRY

It follows from the foregoing that mechanochemical phenomena touch on a wide range of problems of practical interest. The utilisation of mechanochemical processes is proceeding along the following lines.

Intensification of dissolution and leaching processes. The conversion of sparingly soluble substances into a soluble state, usually carried out by heating with concentrated acids or alkali, or by fusion with active components (sodium carbonate, alkali, hydrogen sulphate, etc.) can be accelerated by mechanochemical treatment of the components to be dissolved. An increase in solubility under the influence of mechanochemical treatment is observed for many inorganic substances of practical importance. Data on the increase in solubility under the influence of mechanochemical activation for various substances are given in Table 2.

Increase in the rate of decomposition and synthesis. The problem of increasing the rates of chemical reactions is extremely important, particularly for solid-phase reactions. The reaction product formed at the contact between the granules has a blocking influence on solid-phase reactions. When the reaction is carried out under conditions of intensive mechanical treatment, the reaction product is removed and the surface is renewed, with a consequent significant increase in reaction rate. Moreover, the preliminary mechanochemical treatment of substances not only can provide a means of preparing substances to increase the rate of a reaction, for example with heating, but also can provide an independent and the only possible method of decomposing or preparing substances. Examples of processes which it has been possible to carry out by means of mechanical activation are the preparation of rongalite[126], phosphors[82], metallates[81], organometallic compounds[83], complex compounds[4], catalysts[75,76,127], etc.

Activation of catalysts. On mechanical treatment, the activity of catalysts changes not only as a result of a change in the surface but also as a result of the fact that some of the kinetic energy of the solids in friction is

transferred to the surface. The stresses created in the surface layers are sufficient for breakdown of the structure and rearrangement of the atoms and molecules to form less ordered structures exhibiting a higher potential energy than the ordered crystal structure.

Table 2. Increase in the solubility of inorganic substances under the influence of mechanochemical activation.

Substance	Solvent	Duration of grinding in mill, h	Duration of dissolution, h	Quantity transferred to solution, % of original	Refs.
α-Al_2O_3 (fused)	3*N* NaOH	0	1 (70°)	0	39
		50		8	
		100		14	
		150		22	
		200		28	
SiO_2	H_2O	0	1200	0	28
		0.033		0.10	
		0.066		0.14	
		0.132		0.18	
		0.264		0.27	
SnO_2	18% HCl	12	0.5 (60–80°)	6.9	40
		25		21.2	
		47		29.8	
		72		43.7	
		152		70.0	
		210		80.2	
		300		100	
SnO_2	10% NaOH	12	0.5 (60–80°)	8.7	
		25		25.0	
		47		28.0	
		72		40.4	
		152		63.5	
		210		78.0	
		300		100	
Bauxite (Al_2O_3—48%, Fe_2O_3—22%, SiO_2—7.4%, TiO_2—2.4%)	30% NaOH	0	0.5	3	122
		0.5		22	
		1.0		48	
		2.0		66	
		3.0		72	
		5.0		82	
		7.0		90	
		10.2		100	
Bauxite (Al_2O_3—58%, Fe_2O_3—26%, SiO_2—1%, TiO_2—2%)	30% NaOH	0	2	0.15	29
		20		75	
Kaolin (Al_2O_3—43%, SiO_2—54.2%, K_2O—1.65%)	1 *N* HCl	0	1 (100°)	10	123
		400		20	
		600		40	
		1000		50	
Wolframite (Fe, Mn)WO_4	30% HCl	0	1	32	124
		10		48	
		20		67	
		60		73	
		120		80	
		360		84	
Olive titanomagnetite (Fe_3O_4—27%, $FeTiO_3$—15%)	15*N* H_2SO_4	0	—	34 0	125
		5		60 10	
		30		90 30	
		100		95 60	
		200		95 90	

Study of the catalytic activity of nickel oxide [128] and zinc oxide [129] established that the catalytic activity increases with increase in the degree of subdivision. It was shown that the catalytic activity changes in step with the breakdown of the crystal lattice.

The dependence of the catalytic activity of α-Fe_2O_3 on the duration of mechanical treatment passes through a maximum. According to Schrader [130], the activity of α-Fe_2O_3 at the maximum (grinding for 16 h) in the oxidation of carbon monoxide to carbon dioxide is greater than the activity of the original catalyst by a factor of 5. Analogous data were obtained for catalysts such as copper oxide [131], magnesium oxide [132], alumina [133], etc. [134–137].

The influence of mechanical treatment on the temperature of reduction of oxides has been studied [138]. After treatment for 20 h, the temperature of the start of reduction was decreased by 80 deg for Fe_2O_3, 75 deg for Fe_3O_4, 50 deg for NiO, and 40 deg for CuO.

Mechanical treatment also alters considerably the properties of complex catalysts. It has been shown [139] that prolonged grinding of an aluminosilicate catalyst alters its acidic properties, leading to a decrease in the catalytic activity of the catalyst in the depolymerisation of paraldehyde in benzene solution. Annealing of a catalyst treated in this way leads to the restoration of its activity. Infrared spectroscopic data indicate that water molecules, bonded to the surface by hydrogen bonds, appear on the catalyst surface during size reduction.

The use of mechanochemical treatment for the preparation of new catalysts also appears promising. This method has been used, for example, to prepare a mixed vanadium–molybdenum–aluminium catalyst, used for the oxidation of acrolein, with increased activity and selectivity [75], iron and zinc ferrites [77], etc.

Preparation of substances with new properties. Mechanochemical treatment can be used to solve problems in the modification and improvement of the properties of such substances as adsorbents, zeolites, binding agents, etc. The ability of kaolin to form zeolites on grinding has been studied [140]. It has been established [142] that on dispersion, aluminosilicates are converted into minerals of the kaolinite group. The mechanochemical technology of the production of binding agents from industrial wastes is being developed [143].

Separation of elements with similar properties and the components of complex mixtures. A procedure has been proposed [29] for the extraction of titanium from titanium magnetic ores by mechanical treatment followed by thermal treatment and dissolution in hydrochloric acid. After these operations, TiO_2 passes into solution, and iron(II) oxide is converted into insoluble iron(III) oxide.

A method for separating pyrite and haematite by grinding a mixture of these minerals in the presence of ammonium nitrate has been proposed [72]. On grinding, pyrite is converted into acid-soluble iron sulphate, and haematite remains in the insoluble residue. This operation can be used to separate other substances, for example lead from iron, etc.

Elements with similar properties can also be separated by making use of differences in the rates of their mechanochemical decomposition.

Improvement of existing technological processes. Mechanochemical reactions take place in chemical technology during the size reduction of substances and their mixtures at ordinary temperatures. Little attention has been paid to these reactions until now. For example, before flotation, pyrite is subjected to size reduction in the presence of moisture and atmospheric oxygen. Size reduction is accompanied by the formation of water-soluble oxidation products (sulphates, sulphides, hydroxides, oxides, etc.), and these are lost on flotation [144]. Analogous losses take place in the processing of other mineral products.

Mechanochemical methods of activating a substance in order to increase solubility, separate substances, etc. are also promising in that they make it possible to reduce the consumption of water, a shortage of which has recently been noted. Certain preparations which are usually carried out in aqueous or organic media can be carried out in the solid phase. The reduction of, for example, metals from their sulphides [145] and oxides, etc., can be carried out in this way.

In conclusion it may be noted that despite the fact that the theoretical interpretation of mechanochemical phenomena, because of the complexity of the processes taking place and the restricted nature of the methods for studying them, is extremely far from complete, mechanochemistry has already progressed beyond the trial stage and is providing a means of solving fundamental problems facing chemistry, such as the development of methods for decomposing and preparing substances, and methods for the directed control of chemical reactions.

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Influence of Electronic Interactions with the Carrier and of State of Dispersion of the Metal on the Catalytic Activity of Supported Metal Catalysts

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The application of the metal-semiconductor boundary layer theory to the study of the catalytic properties of supported metal catalysts is discussed. Published work on the structure of very small metal crystals and on anomalous adsorption and catalytic centres in such crystals is discussed with particular reference to the dependence of catalytic activity on the state of dispersion of the metal deposit. 103 references.

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I. INTRODUCTION

The chemistry of catalysis has made important advances during the past 15–20 years, and a deeper understanding of the nature of the catalytic act and of catalyst structure has been acquired by applying new theoretical concepts based on recent advances in solid-state theory, as well as new physical methods of investigation.

The electronic theory of catalysis on semiconductors developed by Vol'kenshtein, Hauffe, and others, and Dowden's use of the concept of *d*-band filling to explain the catalytic properties of transition metals and their alloys, have clearly shown the importance of the collective properties of solids in the field of catalysis.

These ideas have been tested by electrical, magnetic, optical, and other methods, and as a result of this work some new and more precise concepts (involving crystal field and ligand field theories) have emerged. In addition to the collective properties of the solid, the local properties of an individual atom or ion in the lattice (determined by its electronic structure and co-ordination) began to attract attention.

These problems were considered in detail at the Fourth International Congress on Catalysis, held in Moscow, and also in the Symposium on Electronic Phenomena in Catalysis.

This review is concerned with both collective and localised interaction problems in supported metal catalysts, which include a large proportion of all modern industrial catalysts.

Relevant theoretical problems include the mechanism of the interaction between the metal and the carrier, the specific properties of small metal crystals, the relationship between the size and the catalytic activity and selectivity of such crystals, the influence of the carrier on the activity and selectivity of the catalyst, etc.

The past decade has witnessed some important advances in the study of metals on carriers [1], resulting from the development of techniques for the direct examination of disperse metal (magnetic measurements, electron microscopy, X-ray and electron microprobe analysis, CO and H_2 chemisorption). The detailed studies of supported platinum [2,3] and nickel [4–8] on various carriers will be discussed below.

No attempt will be made to review the whole of the work on supported catalysts published during the last few years. We shall deal mainly with the more complex studies of catalysts, which throw light on their structure and physical properties as well as on their precise catalytic activity.

II. ELECTRONIC ASPECTS OF METAL–CARRIER INTERACTION

The role of the carrier in mixed (metal–carrier) catalytic systems has long been thought [9] to be merely structural (protection of the dispersed metal from sintering phenomena, preservation of the large surface area and orientation of the crystals). The development of an electronic approach to catalysis, by Roginskii [10], Vol'kenshtein [11], Hauffe [12], Dowden [13], and others, has brought about a reappraisal of the role of the carrier, for which Schwab and his coworkers [14] have been mainly responsible.

Essentially, the electronic theory of catalysis states that a definite (though indirect) relationship exists between the concentration of current carriers and the Fermi level in the solid on the one hand and the catalytic activity of the solid on the other hand. A change in the semiconductor properties of the carrier, according to Schwab, should produce a corresponding change in the electronic properties of the deposited metal in contact with the semiconductor, and hence it should enhance (or inhibit) the catalytic reaction, since both the catalytic act and its precursor stages (chemisorption of reactants) involve a redistribution of the electron density between catalyst and reacting system.

Schwab's hypothesis was tested experimentally by studying a model reaction of a well characterised type (the dehydrogenation of formic acid). Assuming that the reaction involves electron transfer from the formic acid molecule to the metal, the theory predicts that if the Fermi level in the metal is raised by electronic interaction with the semiconductor the activation energy of the dehydrogenation reaction should increase, and conversely that a decrease in the Fermi level should lower the activation energy of the reaction. Experiments of this type were made by Schwab and coworkers [15] with the following catalysts: metallic nickel, cobalt, and silver, deposited on variously doped (2–5 mol.%) Al_2O_3 samples. Aluminium oxide is an *n*-type semiconductor and is inactive towards the dehydrogenation of formic acid when

heated above 900°C. Addition of oxides of lower-valency metals (NiO, BeO) lowers the electrical conductivity of Al_2O_3, whereas oxides of higher-valency metals (GeO_2 and TiO_2) increase the conductivity. The doped carriers were heated at 1050°, and coated with a thin film of nickel, cobalt, or silver by evaporation in a vacuum. As a control, the dehydrogenation of formic acid was also studied on films of these metals deposited on the corresponding massive metals.

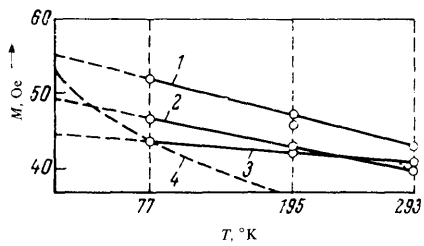

Figure 1. Thermomagnetic curves of Ni on carriers: *1*) Al_2O_3 + NiO; *2*) Al_2O_3; *3*) Al_2O_3 + TiO_2; *4*) shape of the thermomagnetic curve for small nickel particles.

As expected, the activation energy of the reaction was found to be lower than for pure Al_2O_3 on the samples doped with NiO and BeO, and higher on the samples doped with TiO_2 and GeO_2. An attempt was made to demonstrate experimentally the transfer of electrons from TiO_2-doped alumina to the metal by measuring the saturation magnetisation of the nickel and comparing the saturation magnetic moment with that of nickel on pure Al_2O_3. The metal particles were assumed to be very small and in intimate contact with the carrier. The thermomagnetic curves (Fig. 1) of three catalysts were measured: Ni on Al_2O_3, Ni on Al_2O_3 + TiO_2, and Ni on Al_2O_3 + NiO. The curves were measured in the temperature range 77 to 293°K, and extrapolated to 0°K: the magnetic moment was found to be largest on the carrier Al_2O_3 + TiO_2, and smallest on the carrier Al_2O_3 + NiO.

Schwab's next experiment was made with nickel deposited on the *n*-type semiconductor ZnO,[16] doped with Li^+ (which lowers its conductivity) or Ga^{3+} (which increases it). The catalysts were prepared by heating mixtures of the nitrates, and reducing the resulting mixture of oxides to give (according to the authors) very small crystals of nickel in a matrix of ZnO. Another donor reaction was also examined: the hydrogenation of ethylene. The rate of hydrogenation of ethylene (referred to 1 g of nickel) was found to increase when the ZnO contains fewer conduction electrons, i.e. in the presence of Li^+, and to decrease when the concentration of conduction electrons in ZnO is enhanced by adding Ga^{3+}.

Schwab also discusses the ammonia synthesis catalysts[14] from this point of view. He considers that in this case the most important additive is potassium oxide. which has the same effect on Al_2O_3 as BeO,[15] i.e. lowers the concentration of conduction electrons. Since the synthesis of ammonia is a complicated process, the simpler dehydrogenation of formic acid was studied on ammonia synthesis catalysts with and without additions of K_2O. Addition of 1% of K_2O lowers the activation energy from 18 to 13 kcal mole^{-1}, and 2% lowers it to 7 kcal mole^{-1}. Addition of an oxide of higher valency (GeO_2), which increases the conductivity of Al_2O_3, produces the opposite effect: the activation energy increases to 23 kcal mole^{-1}. Thus, Schwab concludes that in the dehydrogenation of formic acid the additives to the Al_2O_3 have an overriding effect both on the electrical conductivity of the alumina and on the catalytic activity of the iron.

Szabo and Solymosi[17] adopted a similar approach to the study of the decomposition of formic acid on Ni–Cr_2O_3 and Ni–TiO_2 catalysts, in which the carriers were doped with ions of different valency (Be, Al, W, Sb, Ni, Cr) in order to alter their conductivity. The pure and the doped carriers were heated at 900°, impregnated with a solution of nickel nitrate, and reduced in hydrogen. Unlike Schwab and his coworkers, these workers determined the extent of reduction of the nickel by measuring the hydrogen evolved on dissolving the catalyst in dilute perchloric acid. The activity was again measured by the activation energy of the dehydrogenation of formic acid. On a pure TiO_2 catalyst the reaction proceeds with an activation energy of 31 kcal mole^{-1}, and on pure Ni the activation energy is 24.6 kcal mole^{-1}. When the Ni is deposited on TiO_2 (in 0.2–3% amounts) the activation energy falls to 22.0 kcal mole^{-1}. Addition of 2% Sb_2O_3 to the carrier raises its electrical conductivity, and the activation energy correspondingly rises by 2 kcal mole^{-1}; addition of 1–5% BeO lowers both the conductivity and the activation energy. Doping the carrier with chromium oxide produced an anomalous result: according to Hauffe Cr_2O_3 increases the conductivity of TiO_2, but Szabo and Solymosi found that the activation energy is lowered. They explain the anomaly by pointing out that the conductivity in this system is affected by the atmosphere in which the measurements are made, and that in a reducing atmosphere the conductivity of titanium dioxide is decreased by doping with chromium oxide, i.e. the Cr^{3+} ions behave like typical lower-valency ions. With Ni–Cr_2O_3 catalysts, on the other hand, addition of titanium dioxide (0.5–5%) to the chromium oxide increases the activation energy and addition of nickel oxide (0.5–5%) lowers the activation energy, with corresponding effects on the electrical conductivity of the carrier. The authors also studied the effect of temperature (400 and 500°) and of time of reduction (1–10 h) on the activation energy of the decomposition of formic acid. In both cases the activation energy increased at 500° and on extending the duration of the reduction. Szabo and Solymosi explain this finding by suggesting that the amount of Ni/NiO in the catalysts decreases as the extent of reduction increases: as previous workers had shown[18], this couple is more active than pure nickel towards the decomposition of formic acid. In the case of Ni–Cr_2O_3 catalysts the resulting spinel is a better carrier for Ni than pure chromium oxide, and the activation energy for the reaction falls to 7 kcal mole^{-1} (for a catalyst containing 5% of NiO) on raising the temperature.

Langenbeck and coworkers[19] studied the effect of *n*-type metal oxides on the catalytic properties of nickel towards the reactions of cyclohexane. They found that the *n*-type oxides ZnO, CdO, TiO_2, and ThO_2 alter the selectivity of the reaction in favour of dehydrogenation to benzene. Several series of preparations were investigated. Initially, zinc oxide was introduced as the third component in Ni–MgO and Ni–Al_2O_3 catalysts at the oxalate or hydroxide coprecipitation stage. The ternary catalysts gave a much higher yield of benzene than the binary catalysts without ZnO. It was subsequently found that a high dehydrogenation activity can be obtained with simple mechanical mixtures of ZnO and the binary catalysts, or by adding zinc powder to the binary catalysts.

Additions of CdO, ThO_2, and TiO_2 were also examined. CdO was very effective at low concentrations, but it was reduced by hydrogen to metallic cadmium at temperatures just above 300°: the cadmium was lost from the bulk of the catalyst by evaporation, and the selectivity reverted to its original value. Addition of TiO_2 and ThO_2 has an appreciable effect only on the $Ni-Al_2O_3$ catalyst, and addition of oxides which are not *n*-type semiconductors (BaO, MgO) has no effect on the properties of nickel. Langenbeck and coworkers, like Schwab, explain these effects by postulating transfer of electrons from the *n*-type oxides to the 3*d* shell of nickel, with the following results: 1) the activation of hydrogen with electron transfer to the nickel, a necessary condition for the degradative hydrogenation of cyclohexane to methane, is prevented by the filling of the 3*d* band of the nickel; 2) the possibility of electron transfer from the cyclohexane molecule to the nickel, with consequent deformation of the chemisorbed molecule and breaking of the C–C bonds, is also excluded. In practice, the observed dehydrogenation (as opposed to degradation to methane) may be due to a combination of these two factors. Another important aspect should be stressed. All promoters are oxides which are partly reduced to metals capable of forming alloys with nickel [20] under the conditions of the reaction: this effect also tends to fill the 3*d* band of the nickel. No clear-cut distinction can be drawn between the electronic effect of the *n*-type semiconductor oxide and the effect of alloying. The main conclusion from this work is that the enhanced selectivity afforded by zinc oxide is due to a change in the electronic properties of the nickel.

Nehring and Dreyer [21] extended this work by studying the reactions of cyclohexane in the presence of a $Ni-Al_2O_3$ catalyst in which the Al_2O_3 was doped with TiO_2 and ThO_2.

They tried to explain the observed dependence of the dehydrogenating activity of the catalyst on the composition of the oxide carrier in terms of the accompanying changes in the electrical conductivity of the carrier. The additions of ThO_2 and TiO_2 were made at the hydroxide coprecipitation stage. The electrical conductivity of the carriers was measured after heat treatment at 1200° (for ThO_2) and 1050° (for TiO_2) because the results obtained after heat treatment at 900° were not reproducible. Measurements of electrical conductivity were carried out in a stream of hydrogen. The conductivity of Al_2O_3 doped with ThO_2 went through a sharp maximum at 1–2% ThO_2, whereas in the $Al_2O_3-TiO_2$ system the conductivity increased continuously with TiO_2 concentration, rapidly at first (up to ~5%) and more slowly up to 100% TiO_2. The nickel was introduced by impregnating the carrier with nickel formate and reducing in a stream of hydrogen (5 wt.%). The decomposition of cyclohexane was studied at 400°: with $Al_2O_3-ThO_2$ catalysts the maximum concentration of benzene in the condensate was obtained with the catalyst containing 10% of ThO_2, and with $Al_2O_3-TiO_2$ catalysts the optimum composition was 1% of TiO_2. Neither of these compositions corresponds to an extremum in the electrical conductivity. The changes in catalytic activity were correlated also with changes in the total surface area of the catalysts. In both systems, the surface area is decreased drastically by small additions of the second oxide, but in the case of TiO_2 the decrease in area occurs in the region of composition corresponding to the maximum yield of the dehydrogenation reaction, whilst in the case of ThO_2 no correlation is found. The lack of correspondence between the maxima in conductivity and in activity is not understood. The results are discussed from the conventional standpoint of changes in the electronic properties of the carrier. It is assumed that the high dehydrogenation activity of Zelinskii and Komarevskii's [22] $Ni-Al_2O_3$ catalyst arises from a modification of the properties of nickel by the conduction electrons of the weakly *n*-type aluminium oxide. Since the addition of higher-valency oxides raises the conductivity of *n*-type semiconductor oxides, the increased selectivity of alumina produced by additions of ThO_2 and TiO_2 is ascribed entirely to this effect.

We have discussed a group of papers characterised by a common approach to the catalytic properties of metals supported on a carrier. Schwab's paper [15], in particular, played a pioneering role in this work and stimulated further research. However, the present writers believe that both the original and the subsequent work contains serious errors.

Firstly, an intimate contact between the phases (i.e. a high degree of dispersion of the deposited metal) is a necessary condition for the postulated, reversible electron transfer between the carrier and the metal. But, as Block pointed out in the discussion of Szabo's paper at the Second Congress on Catalysis [23], even if the metal particles contain as few as 10^3-10^4 atoms the influence of charge transfer on the concentration of electrons and on the position of the Fermi level in the metal is negligibly small. We may consider whether the above condition is fulfilled in the published work. In every case the carrier was heat treated at temperatures of the order of 1000° and, therefore, its surface area was not very great. Hence it is difficult to believe that under these conditions the nickel particles were small enough. Schwab and coworkers [15], assuming their nickel to be very finely divided, quote the effect of additives on the saturation magnetic moment of the nickel as their main evidence for electron transfer from the carrier to the metal. However, the thermomagnetic curves reproduced in Fig. 1 are typical of coarsely divided nickel, and the small difference in the magnetisation of the three catalysts at 77°K (the lowest measurement temperature) is probably due to small differences in the extent of reduction of the metal, which the authors assumed to be 100% without proof. Correct extrapolation to 0°K, with due allowance for the variable extent of reduction, should lead to a single value for the saturation magnetisation, and not three different values as found by the authors. Schwab and Mutzbauer [16] assume that the nickel in their catalysts is present as small particles in a ZnO matrix, but they do not substantiate their claim, which is inconsistent with a recent report [24] that nickel crystals of 360–400 Å diameter are the most stable in a ZnO matrix.

Secondly, all the work discussed attempts to correlate electrical conductivities measured at 900° with activation energies for a chemical reaction at 250–400°. There can be no doubt that the electronic properties of the carrier may be altogether different at the temperature of the catalytic reaction.

Thirdly, the activation energy is not necessarily the best measure of catalytic activity, because of the possibility of compensation which Schwab himself points out [15] without proving that the same kinetic equation applies to all the catalysts used in his experiments. Szabo and Solymosi [17] ascribe significance to changes in E_{act} of 2 kcal $mole^{-1}$, which lie within experimental error, and Langenbeck [19] estimates activity from the percentage conversion of cyclohexane into benzene. Much more reliable means of comparing catalytic activities are needed in order to characterise the more subtle physical effects [25].

Fourthly, no one has considered the direction of electron transfer, i.e. whether the electrons are donated to the conduction band of the metal (where they would have no effect on the magnetic properties), or whether they populate the narrow d_e band (where they would alter the saturation magnetic moment of the Ni atom). Although we do not know whether d electrons (which determine the magnetic properties of ferromagnetic materials) take part in electrical conduction[26], it is important to establish the direction of electron transfer when discussing catalytic activity. If the electron transfer produces a change in the magnetic moment (i.e. an effect analogous to the addition of diamagnetic metals to the nickel), Dowden's theory predicts a decrease in catalytic activity. However, if the electron enters the conduction band there should be no change in the catalytic properties of the nickel, because the resulting contribution to the total number of conduction electrons in the nickel is negligibly small.

In order to understand the physical nature of the charge transfer effect a more detailed consideration of the metal–semiconductor interface is required. We shall assume that an n-type semiconductor (work function φ_S) is in contact with a metal (work function φ_m), where $\varphi_m > \varphi_S$ (see Fig. 2).

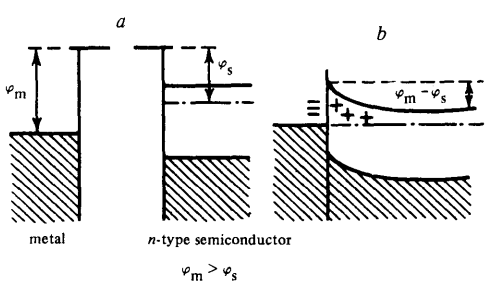

Figure 2. Energy levels at the contact between a metal and an n-type semiconductor: *a*) before contact; *b*) after contact

Since $\varphi_S < \varphi_m$, electrons will pass from the semiconductor into the metal until their chemical potentials (Fermi levels) in the two phases are equal. As a result, the layer of semiconductor immediately adjacent to the metal is depleted of current carriers and becomes positively charged, and the metal becomes negatively charged. The barrier (called a Schottky barrier) which appears at the interface is responsible for contact rectification phenomena.

It is evident from the above that the most important parameter in contact phenomena is not the concentration of current carriers in the semiconductor but the ratio of the work functions in the metal and the semiconductor. Yet, all the published work attempts to correlate catalytic activity with electrical conductivity, and work functions are completely ignored. It certainly cannot be assumed (e.g., in the case of an n-type semiconductor) that the electrical conductivity and the work function must vary in the same sense as a result of doping.

Thus, there are two prerequisites to a correct evaluation of the potential jump which appears at the boundary between the two solid phases: 1) the system must be capable of being described in terms of Schottky's theory[27]†, and 2) the ratio of the work functions in the two phases must be unaffected by interactions with the reacting system. However, even these conditions are necessary but not sufficient. The theory of surface and contact rectification, developed as a branch of semiconductor physics[28], states that the potential barrier at the interface can be modified by the presence of extraneous, poorly conducting layers between the metal and the semiconductor, such as oxide layers (which are termed chemical barrier layers), and also by chemical impurities or lattice defects at the surface (which are termed surface states). Furthermore, doping can have uncontrolled side effects on the catalytic activity by altering the structure type of the lattice, the porosity, and the grain size (i.e. the specific surface area, see Ref. 21). It is clear, therefore, that the state and the properties of the boundary layer in the metal–carrier system are controlled by many factors, and that *a priori* conclusions on the transfer of electrons from the carrier to the metal based only on measurements of the electrical conductivity of the carrier can be of little value. For this reason, attempts are being made to modify the electronic properties of semiconductor catalysts by methods other than doping, e.g. by irradiation with visible and u.v. light during the reaction[29]. Recent data are reviewed by Steinbach[30].

The carriers used by Schwab, Szabo, and Nehring were sintered oxides showing only weak semiconductivity. In the whole of their work the electronic effect of the carrier on the catalytic properties of nickel was only qualitatively assessed. Baddour and Deibert's attempt[31] to demonstrate in a quantitative way the promoting effect of electronic interactions between the carrier and the metal on the decomposition of formic acid is therefore particularly interesting. Germanium, both pure and doped with 0.01% of Zn, Sb, and As, was used as the carrier, to enable the concentration and mobility of the current carriers to be measured by the Hall effect in single crystals of the same composition. Zn-doped germanium becomes a p-type semiconductor, and germanium doped with Sb or As becomes an n-type semiconductor with a known concentration of conduction electrons. The carriers were prepared by grinding Ge single crystals in a vacuum (to avoid atmospheric oxidation). The nickel catalyst was deposited on the carriers by quantitative decomposition of nickel carbonyl. The surface area of the samples was measured (658–1143 $cm^2\ g^{-1}$), and the number of Ni monolayers was calculated (1–18.5). The potential difference at the Ni/Ge interface was calculated by Schottky's theory[27] of contact phenomena at a metal–semiconductor boundary. (A similar calculation[32] for various metals in contact with silicon had given good agreement with experiment). Using the known work functions of Ni (4.96 eV) and Ge (4.78 eV), the authors evaluated the concentration of electrons in the boundary layer of germanium at 240° (the reaction temperature) as 1.4×10^{15}, and also the extent of electron transfer from Ge to Ni for all three dopings. The results are summarised in Table 1.

The activity of pure Ni and Ni/Ge catalysts towards the dehydrogenation of formic acid was studied in a flow reactor at 240 ± 30°, and it was found to decrease with time (particularly in the case of pure nickel). The activity was therefore identified with the initial rate of reaction.

†This condition requires an intimate contact between the two phases and a large area of contact, which are achieved by preparing the metal catalyst in a highly disperse state (see above).

The kinetic order of the reaction (with respect to formic acid) is close to unity on Ni/Ge catalysts and close to zero on pure Ni. As well as the specific reaction rates (per 1 m^2 of total surface area), the authors measured the activation energies and the pre-exponential factors. As the number of Ni layers on the carrier decreases, the activation energy was found to increase sharply from 10 kcal $mole^{-1}$ (for 13–18 layers) to 18–34 kcal $mole^{-1}$ (for 6 and 4 layers respectively). However, due to the compensation effect, the specific reaction rates differed by less than an order of magnitude and increased with the number of atomic layers (for example, for Ni/Ge(Sb) catalysts, from 4×10^{-4} to 22×10^{-4} mole h^{-1} m^{-2} as the number of layers increases from 1 to 18). It is interesting to note that the specific rate of dehydrogenation of formic acid on pure Ni is 3–4 orders of magnitude higher than on supported nickel. The authors compared the specific activities of the three types of Ni/Ge catalyst (doped with Zn, Sb, and As), allowing for the number of layers of deposited nickel (i.e. for the thickness of the metal deposit). Over the thickness range 4–13 layers, the ratio of the activities remained constant (Zn : Sb : As = 1 : 3 : 4). As Table 1 shows, the extent of electron transfer increases in the same order by a factor of 100. The transfer of one electron from the carrier for every 10^5 nickel atoms is found to increase the activity of the metal towards the dehydrogenation of formic acid by a factor of 1.33–3. According to the authors, this indicates that the limiting step in the decomposition of formic acid is dissociative chemisorption, with formation of a negatively charged formate group on the surface (step *1*):

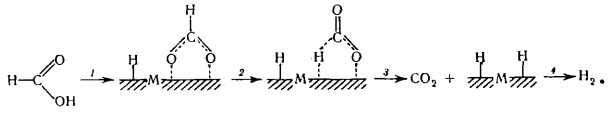

Table 1.

Carrier	Electronic properties	
	Concentration of conduction electrons at 240°, n_s, cm^{-3}	Equilibrium charge transfer at Ni–Ge interface, σ, cm^{-3}
p-type semiconductor		
Zn doped	3×10^{16}	7.3×10^{10}
n-type semiconductor		
Sb doped	3.4×10^{17}	5.3×10^{11}
As doped	2.4×10^{19}	3.7×10^{12}

An electron is transferred from the catalyst to the formic acid molecule. Of course, an increase in the concentration of electrons in the catalyst should assist this step of the reaction. Thus, according to the authors, electron transfer from the carrier to the metal is a very important factor in catalysis. Although their paper describes a well conceived and original physicochemical investigation, an analysis of their results reveals a number of weaknesses. First of all, as the authors themselves point out, effective electronic interaction at the metal–carrier interface requires a large interface area (i.e. a very small metal particle size). This condition does not appear to be fulfilled in their experimental conditions, since the germanium particles have only a moderate surface area (600 to 1100 cm^2 g^{-1}) and it is difficult to believe that the nickel can exist on these coarse particles as very fine crystals. The catalytic activity is related to 1 m^2 of total surface area rather than 1 m^2 of active surface area. The latter, apparently, decreases as the thickness of the deposited layer increases, and therefore the authors' conclusion that the activity increases with the number of layers is not convincing. Furthermore, an increase in catalytic activity by only a factor of 3 is usually interpreted as a constant activity [33,34]. It is also well known that the bulk properties of germanium can differ very substantially from the properties of its surface [35,36], which can be treated as "quasi-isolated". Therefore, Hall measurements of the electronic properties of germanium single crystals [37,38], both pure and doped, may be entirely irrelevant to the electronic properties of the surface of the germanium carrier. Furthermore, the work function of *n*- and *p*-type doped germanium is the same [39]. In any case, the characteristics of the electronic properties of the carriers had been determined before the materials were powdered and coated with nickel. It is well known that fracture can introduce various defects and dislocations in the crystal lattice, leading to the formation of large numbers of surface states which can have a profound effect on the electronic properties of the carrier surface. Lastly, the main conclusion that the transfer of one conduction electron from the carrier per 10^5 nickel atoms can have a significant effect on the catalytic activity is difficult to accept.

As regards the assessment of the catalytic activity, this work is a considerable step forward in comparison with the work of Schwab and Szabo, since the specific reaction rate (rather than the activation energy) is taken as a measure of the activity. But the observed time-dependence of the catalytic activity, and the need to extrapolate the measured rate to zero time, make the comparison of the catalytic and the physical properties of the various materials less than convincing.

Equally unconvincing is the assumption that electron transfer from the semiconducting carrier to the metal (where the concentration of intrinsic conduction electrons is higher by several orders of magnitude) can have a significant effect on the catalytic properties of the metal. Perhaps for this reason, Schwab has recently begun to develop a new approach to the problem: he has used semiconductor catalysts deposited on catalytically inert metals. Thus, the oxidation of CO has been studied on a nickel oxide catalyst deposited on silver [40], and the oxidation of SO_2 on iron oxide deposited on silver alloyed with palladium and mercury [41]. A study has also been reported [35] of the oxidation of methanol in the presence of a ZnO.Ag mixture and of separate samples of ZnO and Ag in various proportions by weight, which show a synergistic effect even when located in different parts of the reactor. In the presence of a metallic carrier the active phase (the semiconductor) is enriched or depleted of current carriers, and this effect controls its catalytic activity. Physical evidence for this hypothesis is provided by the observation, by Schwab and Kritikos [36], that the electrical conductivity of ZnO, NiO, and Cu_2O is affected by the addition of a small percentage of Ag. The latest paper in this series was published in 1969, [42] but a detailed analysis of its results lies beyond the scope of this review.

III. INFLUENCE OF STATE OF DISPERSION AND OF CARRIER ON THE CATALYTIC ACTIVITY OF SUPPORTED METAL CATALYSTS

The relationship between the catalytic activity and the degree of dispersion of the active component is one of the

basic problems of heterogeneous catalysis. In the case of metallic catalysts supported on a carrier, the following questions need to be answered first: whether the catalytic activity depends on the particle size of the deposited metal, whether the formation of a crystal lattice having the properties of the massive metal is a necessary condition for catalytic action, and lastly whether there is an optimum crystallite size giving the maximum catalytic activity. During the 1930's Dankov and Kochetkov [43] studied the hydrogenation of ethylene and the decomposition of H_2O_2 on platinum, and noted a maximum in the activity for a crystal size of 40–50 Å, followed by a rapid fall to zero activity for a diameter of 20 Å. Rubinshtein [44] found the optimum crystal size of nickel on Al_2O_3 for the dehydrogenation of alcohol in the region 60–80 Å. But only recently has a full appreciation of these problems been made possible by careful measurements of the specific catalytic activity per unit area of metal surface, combined with various physical methods of measuring the dispersenes of the metal (electron microscopy, X-ray line broadening, magnetic methods, H_2 and CO chemisorption, etc.). In spite of these advances, the problems are still controversial.

1. Platinum on Carriers

In 1953 Boreskov formulated the hypothesis [33] of constant specific catalytic activity in catalysts of constant chemical composition. He considered the specific activity to be determined mainly by factors such as the chemical composition and the chemical structure of the catalyst. The hypothesis was confirmed by the results obtained by his research team, who found that the specific activity of Pt towards the oxidation of SO_2 [45] and of hydrogen [46] varies by less than an order of magnitude as the specific surface area of the catalyst is varied by 4 orders of magnitude (Pt/SiO_2, and massive platinum in the form of sponge, wire, and foil).

However, the work of Boreskov ignores the influence of the surface structure of the platinum crystals on the catalytic activity. The problem was first formulated by Poltorak, who proposed the "mitohedric method" [47] to deal with it. The method, which is based on a crystallographic description of the co-ordination numbers of the atoms and of the fraction of the atoms in various states within the lattice, involves the following steps. Atoms of three types are considered: 1) atoms associated with microdefects on the surface of large crystals, 2) atoms on crystal edges, and 3) atoms on crystal faces. In order to distinguish their effects, we must compare the specific activities of equilibrium crystals in three regions of crystal size: 10–20 Å (average co-ordination number $\bar{x} < 6$; the atoms are equivalent to microdefects), 20–40 Å ($\bar{x} = 7$, edge elements), and 100–∞ ($\bar{x} = 9$, as on the perfect faces of an infinite crystal). Metal catalysts covering the desired range of crystal size were prepared in the form of platinised silica gels, and the Pt surface area was measured by the hydrogen chemisorption method. Somewhat later, the authors developed the "absolute adsorption isotherm" method [48] of measuring surface area. Many different hydrogenation and dehydrogenation reactions were studied: the hydrogenation of hex-1-ene, cyclohexene, and allyl alcohol [47], the dehydrogenation of cyclohexene [49] and isopropanol [50], the hydrogenolysis of pentane [50], etc. As a result, it was shown that the specific activity of faces, edges, and crystal defects in platinum is approximately constant. Anomalies in the activity were found to be associated not with surface structure, but with changes in the chemical composition of the adsorption layer (oxygen effect, varying degrees of deactivation of the catalyst as a result of secondary reactions, etc.). Poltorak's results appear to confirm Boreskov's hypothesis of constant specific activity [33], with the single exception that Poltorak's experiments dealt with the range of crystal sizes in which the effect of structure on catalytic activity should be apparent (10–50 Å), whereas Boreskov looked for this effect in a region of particle size (> 50 Å) where, according to Poltorak, the effect is normally absent.

In contrast to the results for hydrogenation and dehydrogenation catalysis, studies of the oxidation of ethanol on platinised silica gel revealed a 100-fold decrease in specific activity on changing from a particle size of ~40 Å to 11 Å particles [51]. With particles greater than 40 Å the activity remained constant, and equal to that of platinum black. Thus, crystal faces are the most active elements towards oxidation. It is interesting to note that Poltorak and coworkers did not find a single instance of enhanced activity at edges or crystal defects: this experimental fact is in direct conflict with the widely held belief that co-ordinationally unsaturated atoms in the platinum lattice have a high specific activity.

Boudart and coworkers [34] extended Boreskov's studies of the specific activity of Pt on carriers. They examined a new system—Pt on Al_2O_3, both γ and η forms—in which the platinum is very highly dispersed and the metal particle size can be accurately controlled by raising the temperature at which the catalyst is formed. They showed that the specific activity of their catalysts towards the hydrogenation of cyclopropane was independent of the amount of platinum on the catalyst, of the crystalline form of the alumina, and of the nature of the carrier (Al_2O_3 or SiO_2). By covering the range from highly disperse platinum, in which practically every atom is on the surface, to platinum foil, the specific activity varied by a factor of two whilst the specific surface area varied by 4 orders of magnitude. Thus, in this work, also, we obtain the surprising result that the catalytic activity is "insensitive" to the crystal size, the nature of the carrier, and the method of preparation.

The next paper by Boudart and coworkers [52] was devoted to a study of the catalytic activity of platinum in another reaction: the transformation of neopentane, which in the presence of Pt undergoes isomerisation to isopentane and hydrogenolysis to isobutane and methane. SiO_2, carbon, and η- and γ-Al_2O_3 were used as carriers. The disperseness of the Pt, defined as the ratio of the number of surface metal atoms to the total number of metal atoms, was varied from 3×10^{-2} (for Pt powders) to over 70 (for supported metal). The authors measured the specific activity of the catalysts for both reactions, and obtained the selectivity coefficient s, equal to the ratio of the specific activities for the isomerisation and the hydrogenolysis reaction respectively. The parameter s varied by a factor of 100 for the catalysts examined, the most selective catalysts being Pt on carbon and Pt powder. The selectivity of supported platinum increased with the forming temperature of the catalyst (from 425° to 900°). Following Anderson and Avery [53], the authors explained their results by suggesting that isomerisation occurs through a three-point adsorption of neopentane on the platinum surface, whereas hydrogenolysis involves a transition state showing two-point adsorption. The greater the number of three-atom groupings ("triplets") on the surface, the more predominant isomerisation

becomes as opposed to hydrogenolysis. A geometrical and thermodynamic treatment of the structure and stability of various crystallographic planes of the Pt lattice led the authors to conclude that the greatest number of triplets should be found on a {111} surface, which is the most stable up to 1500°, and also on face edges. Thus, the selectivity should be directly dependent on the disperseness of the platinum and on the heat treatment of the catalyst before the reaction. For example, Pt powder which has been activated in an oxygen atmosphere before being reduced in hydrogen can be expected to have a "rough" surface with a high concentration of triplets: this explains its high selectivity.

Boudart's results on the hydrogenation of cyclopropane are confirmed by the work of Dorling and Moss [3], who studied the hydrogenation of benzene in the presence of a series of Pt/SiO_2 catalysts and observed only a twofold change in the activity of catalysts covering a range of dispersion of two orders of magnitude. Zaidman and coworkers [54-56] studied the specific activity of Pt on Al_2O_3 (as a function of concentration and disperseness of the platinum) towards the dehydrogenation of cyclohexane, and they also found that the activity of the catalyst is unaffected by the disperseness of the platinum.

Other workers (e.g. Sinfelt and coworkers [57] state that the specific catalytic activity of Pt in the dehydrogenation of cyclohexane depends on the nature of the carrier and on the state of dispersion of the metal. Thus, Pt crystals of 10 Å average size (estimated by H_2 chemisorption) were obtained by depositing the metal on Al_2O_3, and 85 Å crystals on alumina–silica. The specific catalytic activity of the highly disperse platinum was the higher by a factor of 6.

Results conflicting with those of Boudart and coworkers [52] were reported also by McKee [58], who showed that the specific activity of platinum black in the propane cracking reaction decreases as the catalyst is sintered.

2. Nickel on Carriers

The effect of state of dispersion on the specific catalytic activity of nickel has been studied in detail by Sinfelt and Carter, and their coworkers: the results have been summarised by Sinfelt [59]. The assumption underlying the whole of this work is that there is no *a priori* reason to expect constant specific activity when the degree of dispersion of the metal is varied over wide limits. Since the proportion of co-ordinationally unsaturated surface atoms in very small particles is large, it is assumed that the electronic properties of small metal particles must differ from those of large crystallites and the massive metals. Furthermore, since the catalytic properties of a supported metal must be largely determined by the electronic properties of its particles, a direct relationship can be expected between the catalytic activity and the particle size of supported metals. Similar views are expressed in the magnetochemical papers of Michel [60], Selwood [61], and others, who state that the Curie temperature of a ferromagnetic metal must be a function of degree of dispersion, and that the exchange interaction parameter in small crystals must be very different from the bulk value: this explains the special electronic properties of small crystals [62]. The theory of ferromagnetism in metals and alloys cannot give an unequivocal answer to the question of the relationship between electronic properties and disperseness, and experimental data on the subject are contradictory. Thus, it is stated in a recent paper [63] that the Curie temperature and the saturation magnetisation of small Ni particles are not significantly different from the values for the massive metal. However, Carter and Sinfelt [64] have shown experimentally that Ni in Ni/SiO_2 catalysts with a low Ni content (1–7%) has a low (paramagnetic) magnetic moment as compared with the massive metal: this observation formed the physical basis of their hypothesis. Sinfelt and his coworkers made a detailed study of the catalytic activity of all the Group VIII metals on various carriers (SiO_2, Al_2O_3, Al_2O_3–SiO_2), using the hydrogenolysis of ethane as a model reaction [4-8,65-68]. Nickel was studied in greatest detail [4-8,65]. An interesting fact was discovered in one of the earliest studies [5]: varying the roasting temperature of NiO/SiO_2 catalysts containing ~10 wt.% of Ni from 100° to 760° has no effect on the specific catalytic activity, although the surface area of the reduced nickel is thereby reduced by a factor of 3. However, the activity could be varied by a factor of 50 by depositing the Ni on different carriers (the highest activity being found with SiO_2, the lowest with alumina–silica) [4], in spite of the fact that the surface of the Ni on the different catalysts varied only by a factor of 2.

A study [7] of the effect of crystal size on the catalytic activity of Ni deposited on silica–alumina showed that the specific activity of the metal is decreased 20-fold by a 3-fold increase in the size of the Ni particles (~30–90 Å).

The same team [6-8] studied also a series of catalysts containing between 1 and 5% of Ni in a highly disperse form on SiO_2 and Al_2O_3–SiO_2. The surface area of the metal was measured by the magnetic method when the hydrogen chemisorption method could not be used (at very low adsorptions) [8]. The catalytic activities and crystallite sizes of the Ni on different carriers are compared in Table 2.

Table 2.

Catalyst	Size of Ni crystals, Å	Specific activity towards hydrogenolysis of ethane
1) Ni on SiO_2		
1% Ni	12	11
10% Ni	24	500
2) Ni on Al_2O_3		
10% Ni	23	260
3) Ni on Al_2O_3—SiO_2		
1% Ni	26	>0.08
10% Ni	29	9.5

The authors stress that the differences in activity are not due to differences in the extent of reduction of the metal, and they suggest that the difference in particle size may itself be the cause of the phenomenon (see above). They put forward the view that small particles have a special activity, irrespective of their large surface area, since the comparison is between specific activities. As Table 2 shows, the enhanced activity of Ni on SiO_2 (as compared with Ni on Al_2O_3–SiO_2) can be ascribed to the higher degree of dispersion of the former catalyst. However, increasing the amount of metal on any one carrier causes both the crystal size and the catalytic activity to increase. The authors conclude that a consideration of crystal size alone is not sufficient to explain their results. The influence of the carrier on the catalytic properties of the metal is a complicated problem, which cannot be formulated exclusively in terms of state of dispersion.

An alternative explanation of Sinfelt's results (Table 2) has recently been put forward by Shephard [69], who suggests that measurements of the active surface of the metal by hydrogen chemisorption may result in misleading values of the specific activity. If the catalyst contains "blocked" pores, accessible to hydrogen but not to the reacting molecule (ethane), too high a value will be obtained for the surface area available for the reaction. But this explanation is tenable only when the specific activity decreases with increase of forming temperature, as in Ref. 7: in this case it is easy to see how the true specific activity can remain constant, or even increase, while the apparent value decreases for the reason given. However, if the specific activity increases [8] (see case 1 of Table 2), the negative correction to the surface area of the metal (to allow for the inaccessibility of narrow pores to the ethane molecule) can only lead to a still higher value of the specific activity. These views are by no means new: a method of measuring effective surface areas by the adsorption of molecules of size comparable to that of the reactant was proposed [70] in 1951.

Yates and Sinfelt [67] obtained interesting results in their study of the catalytic activity of rhodium on SiO_2 towards the hydrogenolysis of ethane as a function of degree of dispersion. The catalysts, containing 0.1–10% of Rh with 11–40 Å particle size, differed in specific activity by no more than a factor of 4, but the most highly dispersed catalysts (0.1–0.3% Rh) had the lowest activity. In contrast to Boudart's results, the activity of massive rhodium and of the samples heated to the highest temperatures (particle size greater than 120 Å) was 20–40 times lower than the activity of the dispersed catalysts. The authors conclude that the region of highest catalytic activity occurs at intermediate degrees of dispersion of the metal.

Catalysts containing nickel on SiO_2 and on alumina–silica have been studied also in the hydrogenation of cyclopropane [71] and of benzene [72]. In the former reaction, as in the hydrogenolysis of ethane, the carrier has a strong influence on the activity and selectivity of the nickel (the reaction can follow two paths: hydrogenation to propane and hydrogenolysis to ethane and methane). Thus, the specific activity of Ni on SiO_2 was 16 times higher than the activity of Ni on Al_2O_3–SiO_2 towards the hydrogenation reaction, and 44 times higher towards the hydrogenolysis reaction. In the latter system, the samples which had been used to study the hydrogenolysis of ethane were examined also for their catalytic activity towards the hydrogenation of benzene. The specific activities of catalysts containing 1 and 10% of Ni on SiO_2 had been found (see Table 2) to be approximately the same, while their particle sizes differed by a factor of 2. This work led the authors to conclude that the activity of Ni/SiO_2 catalysts is independent of the degree of dispersion of the nickel also in the hydrogenation of benzene. The behaviour of Ni/Al_2O_3–SiO_2 catalysts was entirely different. The size of the Ni crystals was practically the same in the two samples (26 and 29 Å, see Table 2), and the activity for benzene hydrogenation decreased sharply as the Ni concentration was lowered to 1%, showing (according to the authors) that the carrier can influence these catalysts. These results confirm the earlier work of Hill and Selwood [73], according to whom the specific activity of Ni/Al_2O_3 catalysts in the same reaction decreases sharply with decrease of Ni concentration in the region of ~ 8%, and preparations containing < 3% Ni are completely inactive (i.e., the finer particles are less active). Conversely, the activity of Ni–SiO_2 catalysts in the region of 1% Ni is indistinguishable, as already stated, from that of the catalysts containing 10% Ni.

We shall consider some other examples of studies of the state of dispersion and catalytic properties of Ni from the standpoint of possible effects of the carrier. Thus, Lyubarskii [74] found that the specific activity of nickel towards the hydrogenation of benzene is constant for the carriers Al_2O_3, Cr_2O_3, and MgO, and also for the catalyst prepared by decomposition of the oxalate or formate.

Nikolaenko and coworkers [75] studied the specific activity of Ni–MgO catalysts prepared by thermal decomposition of the mixed oxalates towards the hydrogenation of benzene, and found a constant activity as the particle size decreased from 3000 Å to less than 17 Å.

Aben and coworkers [76] studied the effect of metal particle size and of the nature of the carrier on the specific catalytic activity (towards the hydrogenation of benzene) of platinum, palladium, and nickel catalysts deposited on SiO_2, Al_2O_3, Al_2O_3–SiO_2, and MgO–SiO_2. The activity, referred to a single surface atom of the metal, was found to be independent of particle size and of the type of carrier.

Dixon and Singh [77] showed, for the same reaction on Ni–Al_2O_3 catalysts covering the wide range of Ni concentrations from 5 to 75%, that the specific activity calculated for 1 m^2 of nickel surface was constant and independent of degree of dispersion.

On the other hand, Swift and coworkers [78], who studied the physical and catalytic properties towards the dehydrogenation of cyclohexane of Ni and Pt deposited by impregnation on η- and γ-Al_2O_3, point out that the activity of Ni (though not of Pt) is affected by the nature of the carrier. These results can be criticised on the grounds that the percentage conversions per unit weight of catalyst and per unit area of catalyst surface were both taken as a measure of the activity. Thus, the Ni–γ-Al_2O_3 catalyst, which had almost twice the area of active phase of the Ni–η-Al_2O_3 catalyst and had a greater activity as judged by the percentage conversion, was found to be the less active when the results were recalculated for 1 m^2 of catalyst area.

Van Hardeveld and Hartog [79] studied Ni catalysts on Aerosil with different mean particle size and size distribution. By measuring the intensity of the i.r. absorption bands of adsorbed N_2, CO, and CO_2 molecules they were able to evaluate the proportion of active centres (defined below) on the nickel surface, and to compare this quantity with the activity and selectivity of the catalyst in the exchange and deuteration reactions of benzene. These workers showed that the ratio of the exchange and deuteration rates and the initial isotopic composition of the benzene are very sensitive to the type of catalyst. High activity in exchange reactions results from the presence of large crystallites, and is most probably associated with defects in such particles. This effect almost exactly balances the decrease in the number of surface atoms with decreasing crystal size, and as a result the Ni surface remains uniform towards the deuteration reaction. Thus, the size of the crystals is found to be of fundamental importance in determining the activity and selectivity of the catalysts.

As the above examples show, in most comparative studies of catalytic activity and selectivity the specific surface area of the metal is treated as a simple parameter, and the distribution of particle sizes is ignored. More latterly, as a result of the growing interest in the properties of small particles, more detailed discussions of the nature of active centres in catalysts containing very

finely divided metals on a carrier have been published [80-82]. A basic investigation by van Hardeveld and van Montfoort[80] deals with the influence of crystal size on the adsorption of molecular nitrogen on Ni, Pd, and Pt. It is shown that the stretching vibration of the nitrogen molecule is active in the infrared spectrum only when the N_2 is adsorbed at some special sites on the surface. These centres are present in significant numbers only in small crystals ($20 < d < 70$ Å), and have a co-ordination number of 5 (B_5 centres): an atom adsorbed on such a centre is in contact with 5 Ni atoms. The particle size of the Ni–SiO_2 catalysts was measured by electron microscopy. The authors examined models of particles with different numbers of atoms, in the form of perfect or incomplete cubo-octahedra. The former are bounded exclusively by {111} and {100} surface planes: B_5 centres are absent, and the co-ordination number of adsorbed atoms is 3 or 4 for the two planes respectively.

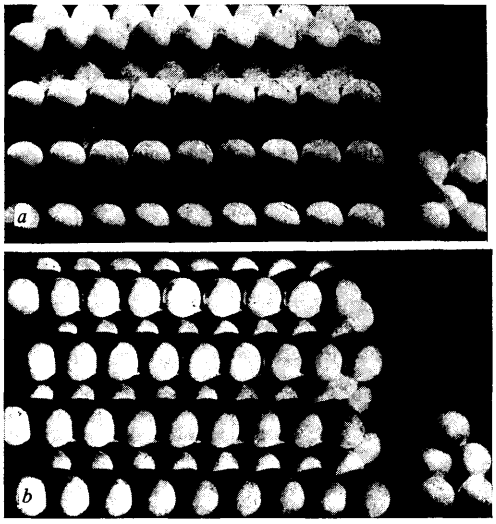

Figure 3. Models of defect planes containing B_5 centres: *a*) {110} plane; *b*) {113} plane. The configurations of the two types of B_5 centre are shown on the right.

In the second model, the less densely packed {113} and {110} planes are present as well as the {100} and {111}; these introduce two geometrically distinct types of B_5 centre (Fig. 3). The authors used a mathematical method of calculating the maximum number of B_5 (and also B_3 and B_4) centres as a function of crystal diameter, and they obtained distribution curves for the three types. B_5 centres are absent in very small particles ($d < 10$ Å), and also in particles with $d > 40$–50 Å, and their probability of occurrence is a maximum in the region 18–25 Å. The adsorption of molecular nitrogen on Ni, Pt, and Pd, first observed by Eischens and Jacknow[83], is discussed in detail in the same paper. Although the relatively high heat of adsorption (12 kcal $mole^{-1}$) suggests that we are dealing with chemisorption, the authors conclude from the lack of specificity of the phenomenon that adsorption on noble metals is physical. The main conclusion of the work is the following. Before making any statement as to the influence of current carriers on the catalytic and chemisorption properties of a metal, as revealed for example by changes in the spectra of adsorbed molecules (cf. the work of O'Neil and Yates[84] on nickel catalysts and of Eishens[85] on platinum), we must examine the distribution of particle size, which is determined first and foremost by the nature of the carrier. The number of B_5 centres, and hence the relative contribution of "defect" planes to the total metal surface, can be evaluated from the intensity of the absorption bands of adsorbed nitrogen. This approach was mentioned above when discussing the work of van Hardefeld and Hartog[79] on the deuteration and exchange reactions of benzene on a nickel catalyst.

Schlösser[81] extended the work of van Hardeveld and van Montfoort[80] on the number of B_5 centres in various cubo-octahedral models. He considered models of cubo-octahedra having different symmetries and defect structures, and he discussed in particular the forms obtained by cutting the corners and edges of a simple cubo-octahedron in various proportions and which can be expected to exist in real catalysts. He showed that the appearance of new low-index planes such as {311}, {210}, etc. increases the number of active B_5 centres, and he compared the number of B_5 centres and the catalytic activity for a number of systems described in the literature.

The paper presented by Bond to the Fourth International Congress on Catalysis[82-85] discusses the same problem from the standpoint of the influence of B_5 centres on the mechanism of various catalytic reactions.

When comparing the activity of a series of catalysts with their degree of disperseness it is important to note that the particle size of the metal can change in the course of the reaction, because of the increased mobility of certain atoms. For example, the size of the Pd crystals varied from 65 Å to 1300 Å, even at 40°, during the hydroisomerisation of but-1-ene on a Pd–graphite catalyst[86]. Obviously, the number of active (e.g. B_5) centres measured prior to the catalytic reaction may also be affected by the exposure of the catalyst to the reaction system. It is very important, therefore, to study the physical properties of the catalyst after, as well as before, the reaction as in the work of Rubinshtein and coworkers[24].

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In spite of the variety of apparently contradictory information on the influence of state of dispersion, and type of carrier, on the catalytic activity of metals, there is a general trend which allows us to systematise the existing knowledge and to formulate profitable objectives for future investigations. The first explicit statement of the correct approach to the problem was made by Boudart and coworkers[34], whose results are discussed on p. 865. It is proposed that all catalytic reactions be divided into two classes: "unhindered" [facile] and "hindered" [demanding]. In the former the active centres have approximately the same activity, and the specific activity is independent of particle size and of the method of preparation of the catalyst (as in Ref. 34). The second class includes reactions which require special configurations of surface atoms, produced by optimising the catalyst preparation procedure. Hindered reactions are invariably sensitive to the size of the metal particles, to heterogeneity of the catalyst surface, and to the type of carrier. Boudart's classification of catalytic reactions shows some obvious similarities with Balandin's views on

the role of the geometric factor in catalysis. As Boudart himself points out, similar ideas were put forward much earlier by Taylor [87], who stated that the catalytically active fraction of the surface is determined by the catalytic reaction in progress. Boudart stresses that the model reactions chosen for systematic studies of catalysts must not be of the hindered type. Reliable correlations between the activity and the structure of the catalyst can be expected only for reactions known to be free from structural complications. In addition to the reactions of neopentane on platinum [52], Boudart discusses other examples of reactions of both types which had been previously studied by Kemball and coworkers [88] on nickel catalysts and by Kral [89] on palladium deposited on carbon.

Table 3. Dependence of activity on state of dispersion for supported metal catalysts.

Reaction	Catalyst	Dependence on		Refs
		state of dispersion of metal	nature of carrier	
Oxidation of SO_2	Pt, Pt/SiO_2	no	no	45
Oxidation of H_2	Pt, Pt/SiO_2	no	no	46
Hydrogenation of benzene	Ni, Ni/Cr_2O_3, Ni/MgO	no	no	79
	Ni/SiO_2, Ni/Al_2O_3, Ni/C, $Ni/Al_2O_3 \cdot SiO_2$, $Ni/MgO \cdot SiO_2$			74–76, 90–92
	Co/SiO_2, Co/Al_2O_3, Co/C $Co/Al_2O_3 \cdot SO_2$	no	no	93
	Pt/SiO_2, Pt/Al_2O_3, $Pt/Al_2O_3 \cdot SiO_2$, $Pt/MgO \cdot SiO_2$	no	no	3, 76
	Pd/SiO_2, Pd/Al_2O_3, $Pd/Al_2O_3 \cdot SiO_2$, $Pd/MgO \cdot SiO_2$	no	no	76
Dehydrogenation of cyclohexane	Ni/SiO_2, Ni/Al_2O_3, $Ni/Al_2O_3 \cdot SiO_2$	no	no	78, 93
	Pt/Al_2O_3, $Pt/Al_2O_3 \cdot SiO_2$	no	no	54–57, 94, 95
Hydrogenation of phenol	Ni, Ni/Al_2O_3, Ni/ZnO, Ni/NiO	no	no	96
Hydrogenation or hydrogenolysis of cyclopropane	Ni/SiO_2, $Ni/Al_2O_3 \cdot SiO_2$	no	yes	72
	Pt/SiO_2, Pt/Al_2O_3	no	yes	34
Hydrogenolysis of ethane	Ni/SiO_2, Ni/Al_2O_3	no, or positive effect*	yes	4, 5, 7
	$Ni/Al_2O_3 \cdot SiO_2$		yes	
H–D exchange in $C_6H_6 + D_2$ mixture	Co/SO_2, Co/Al_2O_3, $Co/Al_2O_3 \cdot SiO_2$		yes	97
	Ni/SiO_2	negative effect		80
Hydrogenation of CO_2	Ni/Cr_2O_3	no		98, 99
Dehydrogenation of n-hexane	Pt/Al_2O_3	no		100
Isomerisation of n-hexane	Pt/Al_2O_3	no		
Hydro-cracking of n-heptane	Pt/Al_2O_3	transition from positive to negative effect	yes	95, 101
Dehydrocyclisation of n-heptane	Pt/Al_2O_3	no		
Isomerisation of n-heptane	Pt/Al_2O_3	negative effect		
Hydrogenation of heavy oil	Pt/Al_2O_3	no	yes	102
Hydro-cracking of heavy oil	Pt/Al_2O_3	transition from positive to negative effect		
Hydrocyclisation of methylcyclopentane	Pt/Al_2O_3	negative effect		103

*The terms "positive" or "negative" effect are used in the meaning of the classification proposed by Bond to the Fourth International Congress on Catalysis, Moscow, 1968.

For example, the deuteration of ethylene on nickel is unhindered, in contrast to the deuterium exchange of alkylbenzenes. As stated above, the hydrogenation of benzene [75–77] is an unhindered reaction (unexpectedly so, in the light of the sextet mechanism of the reaction). However, Bond has pointed out [82] that the formation of olefins by the partial hydrogenation of aromatic compounds was reported at the Third International Congress on Catalysis: this suggests the possibility of a doublet mechanism. Van Hardeveld and Hartog [79] had generally assumed that adsorbed molecules of benzene are attached to a single nickel atom, with formation of a surface compound of the π-complex type. This view is consistent with the experimental fact that the hydrogenation of benzene is unhindered. On the other hand, reactions involving linear molecules such as paraffin hydrocarbons (e.g. the hydrogenation of ethane, studied by Sinfelt and coworkers) are of the hindered type. Schlösser [81] has published a detailed analysis of the available data, summarised in Table 3, in the light of Boudart's classification. In the present state of knowledge if is not yet possible to account for all the known facts, or to predict whether the specific activity of the supported catalyst in various types of reaction should be a function of particle size or of the nature of the carrier. However, the present approach, based on the conformation of the reacting molecules and on the geometry of the assumed active centres, is much more successful than the earlier "electronic" concepts on the influence of the carrier on the properties of the metal.

Therefore, we conclude that the most important problem facing experimentalists at the moment is to compare catalytic activities (preferably, in various types of reaction) with the average particle size and also with the particle size distribution of the catalyst. Reliable information of this type must be made available before further progress can be made towards a full understanding of the nature of the catalytic action of supported metals.

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Quantitative Aspects of the Mechanism of Reactions Involving Hydrocarbons

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This review attempts to generalise a method of evaluating the contributions to the heat of formation of hydrocarbons and their halogen derivatives based on modern views on the structure of the carbon atom. This approach throws new light on the mechanism of a number of reactions, and on the nature of the activation energy of these processes. 88 references.

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1. INTRODUCTION

The mathematical difficulty of exact calculations based on quantum theory[1-6], the complexity of atomic structures, and the wide variety of organic compound have given rise to a great deal of pessimism on the prospect of obtaining exact information useful to experimental chemists, in spite of the advent of electronic computer techniques. However, there is little doubt (in view of the many experimentally observed correlations) that relatively simple methods of solving these problems must exist. The need for simple computational methods arises on the one hand because of the large number of such computations envisaged, and on the other hand from the fact that many of the problems are only of passing interest. For this reason, semi-empirical methods are being applied on an increasing scale in various branches of chemistry[7-13], including quantum chemistry[14-17]. Descriptive (though not strictly accurate) concepts are often more useful to the practical worker than complicated and fully developed physical models. For example, the electronegativity concept[18-22] has played an important role in the development of chemical thinking in spite of the many criticisms which have been levelled at it.

This article aims to review the ideas which enable the heats of formation of hydrocarbons and their halogen derivatives to be correlated with structural parameters[23-26]. The proposed semi-empirical method for calculating heats of formation differs from alternative approaches[7-9,27,28] in its basic principles, and it allows calculation of the heats of formation not only of hydrocarbon molecules but also of their gaseous radicals and their halogen derivatives of practically any structure. Thus, the method is of value in the quantitative discussion of reaction mechanisms[29-32].

2. CONTRIBUTIONS TO THE HEAT OF FORMATION OF HYDROCARBONS

We shall make the following assumptions: 1) the energy of a covalent bond between two atoms is a constant, depending only on the chemical nature of the atoms involved; 2) the energy evolved when electrons become hybridised is determined by the form of the hybridisation of the orbitals; 3) hydrogen (or halogen) atoms combined with carbon atoms develop a constant charge, and the charge on the carbon atom is equal and opposite to the sum of the charges on these atoms. If these assumptions are true, the heat of formation (ΔH) of any gas-phase molecule or radical C_nH_p is given by the expression

$$\Delta H_{C_nH_p} = n_1\Delta H_{C'} + (n - n_1)\,\Delta H_C + p\Delta H_H - pE_{C-H} - wE_{p^3} - fE_{sp^3} - gE_{sp^2} - hE_{sp} - sE_{C-C} - tE_{C=C} - uE_{C\equiv C} - m\sum_{i=1}^{n} a_i^2 \quad (1)$$

where $\Delta H_{C'}$, ΔH_C, and ΔH_H are respectively the heats of formation of a bivalent and a quadrivalent carbon atom from graphite, and of a hydrogen atom from its molecule; n_1 and p are the numbers of bivalent carbon atoms and hydrogen atoms respectively; E_{C-H}, E_{C-C}, $E_{C=C}$, and $E_{C\equiv C}$ are the energies of the covalent C–H, C–C, C=C, and C≡C bonds; s, t, and u are the numbers of C–C, C=C, and C≡C bonds; E_{p^2}, E_{sp^3}, E_{sp^2} and E_{sp} are the energies involved in p^2, sp^3, sp^2, snd sp hybridisation of the electrons; w, f, g, and h are the number of carbon atoms in p^2, sp^3, sp^2, and sp states of orbital hybridisation; $\sum_{i=1}^{n}$ denotes summation over values of i from 1 to n; a is the number of hydrogen atoms on the i-th carbon atom; m is the energy of the electrostatic attraction between a hydrogen atom and a carbon atom with an equal and opposite charge.

The last term of Eqn. (1) relates exclusively to the electrostatic interaction of the carbon atoms with the hydrogen atoms directly attached to them.

Applying Eqn. (1) to the heats of formation of methane, ethane, ethylene, and acetylene, and using these values to calculate the enthalpy of formation of a hydrocarbon molecule without conjugated double bonds, for which $n - n_1 = f + g + h = s + t + u + 1$, we obtain

$$\Delta H_{C_nH_p} = s\Delta H_{C_2H_6} + (f - 2s)\,\Delta H_{CH_4} + t\Delta H_{C_2H_4} + u\Delta H_{C_2H_2} + m\,(16f - 14s + 8t + 2u - \sum_{i=1}^{n} a_i^2). \quad (2)$$

This equation makes no allowance for possible conjugation of double bonds, which produces additional stabilisation energy, or for bond strain resulting from distortion of the bonds from their normal directions [24].

For the special case of gaseous paraffin hydrocarbons with an unbranched chain (C_nH_{2n+2}), Eqn. (2) takes the simpler form

$$\Delta H_{C_nH_{2n+2}} = (n-1)\,\Delta H_{C_2H_6} + (2-n)\,\Delta H_{CH_4} + (2-n)\,2m\,. \qquad (3)$$

Table 1. Heats of formation of gaseous hydrocarbons under standard conditions.

Formula	Compound	ΔH, kcal mole^{-1} corrected (Refs.9,28, 33,34)	ΔH, kcal mole^{-1} calculated by Eqn.(2)	$\Delta H_{calc} - \Delta H_{corr}$ kcal mole^{-1}
1	2	3	4	5
C_4H_{10}	Butane	−30.15	−30.09	+0.06
C_7H_{16}	Heptane	−44.89	−44.88	+0.01
$C_{10}H_{22}$	Decane	−59.67	−59.67	0.00
$C_{13}H_{28}$	Tridecane	−74.45	−74.46	−0.01
$C_{16}H_{34}$	Hexadecane	−89.23	−89.24	−0.01
$C_{19}H_{40}$	Nonadecane	−104.00	−104.03	−0.03
C_4H_8	But-1-ene	−0.03	+0.06	+0.09
C_7H_{14}	Hept-1-ene	−14.89	−14.73	+0.16
$C_{10}H_{20}$	Dec-1-ene	−29.67	−29.52	+0.15
$C_{13}H_{28}$	Tridec-1-ene	−44.45	−44.30	+0.15
$C_{16}H_{32}$	Hexadec-1-ene	−59.23	−59.09	+0.14
$C_{19}H_{38}$	Nonadec-1-ene	−74.00	−73.88	+0.12
C_4H_6	But-1-yne	+39.48	+39.17	−0.32
C_7H_{12}	Hept-1-yne	+24.62	+24.38	−0.24
$C_{10}H_{18}$	Dec-1-yne	+9.85	+9.60	−0.25
$C_{13}H_{24}$	Tridec-1-yne	−4.93	−5.19	−0.26
$C_{16}H_{30}$	Hexadec-1-yne	−19.71	−19.98	−0.27
$C_{19}H_{36}$	Nonadec-1-yne	−34.49	−34.76	−0.27
C_6H_{14}	Hexane	−39.96	−39.95	+0.01
C_6H_{14}	2-Methylpentane	−41.66	−42.53	−0.87
C_6H_{14}	3-Methylpentane	−41.02	−42.53	−1.51
C_6H_{14}	2,3-Dimethylbutane	−42.49	−45.12	−2.63
C_6H_{14}	2,2-Dimethylbutane	−44.35	−47.70	−3.35
C_6H_{10}	Pent-1-ene	−5.00	−4.87	+0.13
C_5H_{10}	*Cis*-pent-2-ene	−6.71	−7.46	−0.75
C_5H_{10}	*Trans*-pent-2-ene	−7.59	−7.46	+0.13
C_5H_{10}	3-Methylbut-1-ene	−6.92	−7.46	−0.54
C_5H_{10}	2-Methylbut-2-ene	−10.17	−12.62	−2.45
C_5H_8	Pent-1-yne	+34.50	+34.24	−0.26
C_5H_8	Pent-2-yne	+30.80	+29.08	−1.72
C_5H_8	2-Methylbut-3-yne	+32.60	+31.66	−0.94
C_5H_8	1,4-Pentadiene	+25.20	+25.28	+0.08
C_6H_{10}	Cyclohexane*	−29.43	−29.57	−0.14
C_7H_{14}	Methylcyclohexane	−36.99	−37.08	−0.09
C_8H_{16}	Ethylcyclohexane	−41.05	−42.01	−0.96
C_8H_{16}	*Cis*-1,3-diemthylcyclohexane	−44.16	−44.60	−0.44
C_6H_{10}	Cyclohexene	−1.70	−2.01	−0.31
C_8H_8	Cyclooctatetraene**	+71.12	+70.84	−0.28

* The carbon atoms of the cyclohexane molecule are not coplanar [35,36]; as a result, the bonds are unstrained.
** The carbon atoms in the cyclooctatetraene molecule lie in different planes [35,38]. This may explain the absence of a conjugation effect.

By inserting known values [9,28,33,34] of ΔH into Eqn. (3) it can be shown that $m = 1.291$ kcal mole^{-1}. Knowing m, Eqn. (2) can be used to calculate the enthalpies of formation of various gaseous hydrocarbons [23,24], saturated or unsaturated, aliphatic or cyclic. The precision of some of these calculations is illustrated in Table 1: evidently, there is a loss of precision when the carbon chain is branched. Eqn. (2) can be used to calculate approximate enthalpies of formation not only at the standard temperature [26]. It can be used also to evaluate [24] the effect of strain in cyclic molecules due to distortion of the bonds from their normal tetrahedral angles [35-37], and the energy of conjugated double bonds due to π-bond delocalisation [5,6,35-37].

3. QUANTITATIVE EXPRESSIONS FOR THE CONTRIBUTIONS TO THE HEATS OF FORMATION

It is experimentally known [27,34] that an expenditure of 80 kcal mole^{-1} is needed to abstract the hydrogen atom from a diatomic CH particle in which the carbon atom is bivalent and the electrons are not in any way hybridised. Since the electrostatic attraction energy between the C and H atoms in this case is m, it follows that the energy of the covalent C−H bond is $E_{C-H} = 78.71$ kcal mole^{-1}.

Also, applying Eqn. (1) to the experimental values for the heats of formation of methane, methyl, and allene (−17.889 kcal mole^{-1} [33,34], +31.5 kcal mole^{-1} [33,39], and +45.92 kcal mole^{-1} [33,34] respectively), we can easily show that

$$\Delta H_C - E_{sp^3} = 109.25 \text{ kcal mole}^{-1}\,, \qquad (4)$$

$$\Delta H_C - E_{sp^2} = 122.98 \text{ kcal mole}^{-1}\,, \qquad (5)$$

$$\Delta H_C - E_{sp} = 150.04 \text{ kcal mole}^{-1}\,. \qquad (6)$$

Since the heat of formation of a gaseous carbon atom in the ground state (C′) from graphite is $\Delta H_{C'} = 171.698$ kcal mole^{-1} [34], we obtain the value $E_{p^2} = 47.3$ kcal mole^{-1} [24] for the p^2-hybridisation energy by taking the heat of formation of methylene as 66 kcal mole^{-1} [27,40]. Using Eqns. (4)−(6) and the enthalpies of formation of ethane, ethylene, and acetylene we arrive at $E_{C-C} = 55.9$ kcal mole^{-1}, $E_{C=C} = 116.6$ kcal mole^{-1}, and $E_{C\equiv C} = 190.1$ kcal mole^{-1}. Eqns. (4)−(6) also show that the energy of sp^3-hybridisation of the orbitals of a quadrivalent carbon atom is greater than the energy of sp^2-hybridisation by 13.7 kcal and is greater than the energy of sp-hybridisation by 40.8 kcal.

Thus, since $n - n_1 = f + g + h$, all the quantities which appear in Eqn. (1) are known, and they can be used in principle for approximate calculations of the heats of formation of gaseous hydrocarbon molecules or radicals free from conjugation or strain effects. However, simpler and more accurate methods [7-9,27,28,34] are available for calculating the heat of formation of molecules, including our Eqn. (2). Hence, Eqn. (1) is most effectively used, in conjunction with Hess's law, to calculate the thermochemistry of reactions involving hydrocarbon radicals, and also to evaluate the heats of formation of the radicals.

4. HEATS OF SOME REACTIONS BETWEEN HYDROCARBON MOLECULES AND RADICALS

a. Hydrogen Atom Removal Reactions

All the carbon atoms in paraffin hydrocarbon molecules are in the sp^3 state of orbital hybridisation. When a combined hydrogen atom is removed, the carbon atom passes from the sp^3 to the sp^2 form of electron hybridisation, and at the same time the electrostatic contribution to the C−H bond energy of the carbon atom changes. The heat of this reaction (Q_1) is given by Eqn. (1) and Hess's law in the form

$$Q_1 = E_{C-H} + E_{sp^3} - E_{sp^2} + m\,(2a-1) \qquad (7)$$

where a is the number of hydrogen atoms bound to the original carbon atom [30].

Similarly, when a hydrogen atom is removed from an unsaturated molecule containing a double bond, the reacting

carbon atom passes from the sp^2 to the sp hybridisation form, and the heat of the reaction (Q_2) is given by

$$Q_2 = E_{C-H} + E_{sp^3} - E_{sp} + m(2a - 1) . \quad (8)$$

The heats of a number of reactions in which hydrogen atoms are removed from hydrocarbon molecules and radicals, calculated in this way, are listed in Table 2. Where experimental values exist, the agreement is satisfactory.

Table 2. Heats of hydrogen atom removal from hydrocarbon molecules and radicals.

No.	Reaction	State of carbon atom: initial V	initial H	final V	final H	Q, kcal mole^{-1}: calc.	exper. (Ref.41)
	Removal of H from molecules						
1	$CH_4 \rightarrow CH_3 + H$	4	sp^3	4	sp^3	101.5	103±2
2	$-CH_3 \rightarrow -CH_2 + H$	4	sp^3	4	sp^3	98.9	97±1
3	$>CH_2 \rightarrow >CH + H$	4	sp^3	4	sp^3	96.3	94±2
4	$\diagup\!\!>CH \rightarrow \diagup\!\!>C + H$	4	sp^3	4	sp^3	93.7	89±2
5	$=CH_2 \rightarrow =CH + H$	4	sp^2	4	sp	109.6	104
6	$\diagdown\!\!>CH \rightarrow \diagdown\!\!>C + H$	4	sp^2	4	sp	107.0	—
	Removal of H from radicals						
7	$CH_3 \rightarrow CH_2 + H$	4	sp^2	4	sp	112.2	—
8	$CH_3 \rightarrow CH_2 + H$	4	sp^2	2	p^2	86.6	85±7
9	$-CH_2 \rightarrow -CH + H$	4	sp^2	4	sp	109.6	—
10	$-CH_2 \rightarrow -CH + H$	4	sp^2	2	p^2	84.0	—
11	$>CH \rightarrow >C + H$	4	sp	4	sp	107.0	—
12	$>CH \rightarrow >C + H$	4	sp^2	2	p^2	81.4	—
13	$=CH \rightarrow =C + H$	4	sp	2	—	101.7	—
14	$CH_2 \rightarrow CH + H$	2	p^2	2	—	129.9	128±6
15	$-CH \rightarrow -C + H$	2	p^2	2	—	127.3	—

Note. V = valency, H = hybridisation.

Tatevskii has pointed out[42] that the distinction between molecules and radicals is to some extent arbitrary. Therefore, the following reasoning may be justified. Reactions 7, 9, and 11 (Table 2) give rise to "hot" particles, containing an excess of energy as compared with the bivalent state of the carbon atom with p^2 hybridisation (reactions 8, 10, and 12 of Table 2). However, since the rate of collisions between gas-phase particles can be as high as 10^{28} per second[43,44] [sic!, 10^{10} at one atm. is more reasonable, (Ed. of Translation)], the excess of energy is quickly dissipated[45], and these "hot" particles have no practical existence.

b. Hydrogen Atom Exchange Reactions Involving Radicals

Using Eqn. (1) and Hess's law, we obtain the following expression for the heat (Q_3) of hydrogen atom exchange reactions involving radicals, in which the reacting carbon atoms are in the sp^3 hybridisation and the sp^2 hybridisation in the initial molecule and radical respectively (Table 3, reactions 1–4, 7–9, 12, 13, 16):

$$Q_3 = 2m(a - a_1 - 1) \quad (9)$$

where a and a_1 are the numbers of hydrogen atoms on the reacting carbon atoms of the original molecule and radical respectively.

When the reacting carbon atoms in the radical and the molecule have the same (sp^3) hybridisation, as in reactions 5, 6, 10, 11, 15, 17, 18 of Table 3, the heat of the reaction (Q_4) is given by

$$Q_4 = 2E_{sp^3} - E_{sp^3} - E_{sp} + 2m(a - a_1 - 1) \quad (10)$$

Table 3. Heats of radical reactions involving hydrogen exchange and biradical formation.

No.	Reaction	Q, kcal mole^{-1}
	H atom exchange reactions (Ref.31)	
1	$CH_3 + CH_4 \rightarrow CH_4 + CH_3$	0
2	$CH_3 + CH_3- \rightarrow CH_4 + CH_2-$	−2.6
3	$CH_3 + CH_2\diagup \rightarrow CH_4 + CH\diagup$	−5.2
4	$CH_3 + CH\diagup\!\!\diagup \rightarrow CH_4 + C\diagup\!\!\diagup$	−7.7
5	$CH_3 + CH_2 = \rightarrow CH_4 + CH=$	+8.1
6	$CH_3 + CH\diagup\!\!= \rightarrow CH_4 + C\diagup\!\!=$	+5.6
7	$-CH_2 + CH_3- \rightarrow -CH_3 + CH_2-$	0
8	$-CH_2 + CH_2\diagup \rightarrow -CH_3 + CH\diagup$	−2.6
9	$-CH_2 + CH\diagup\!\!\diagup \rightarrow -CH_3 + C\diagup\!\!\diagup$	−5.2
10	$-CH_2 + CH_2 = \rightarrow -CH_3 + CH=$	+10.7
11	$-CH_2 + CH\diagup\!\!= \rightarrow -CH_3 + C\diagup\!\!=$	+8.1
12	$>CH + CH_2\diagup \rightarrow >CH_2 + CH\diagup$	0
13	$>CH + CH\diagup\!\!\diagup \rightarrow >CH_2 + C\diagup\!\!\diagup$	−2.6
14	$>CH + CH_2 = \rightarrow >CH_2 + CH=$	+13.3
15	$>CH + CH\diagup\!\!= \rightarrow >CH_2 + C\diagup\!\!=$	+10.7
16	$\diagup\!\!>C + CH\diagup\!\!\diagup \rightarrow \diagup\!\!>CH + C\diagup\!\!\diagup$	0
17	$\diagup\!\!>C + CH_2 = \rightarrow \diagup\!\!>CH + CH=$	+15.9
18	$\diagup\!\!>C + CH\diagup\!\!= \rightarrow \diagup\!\!>CH + C\diagup\!\!=$	+13.3
19	$H + CH_4 \rightarrow H_2 + CH_3$	−2.7
20	$H + CH_3- \rightarrow H_2 + CH_2-$	−5.3
21	$H + CH_2\diagup \rightarrow H_2 + CH\diagup$	−7.8
22	$H + CH\diagup\!\!\diagup \rightarrow H_2 + C\diagup\!\!\diagup$	−10.4
23	$H + CH_2 = \rightarrow H_2 + CH=$	+5.4
24	$H + CH\diagup\!\!= \rightarrow H_2 + C\diagup\!\!=$	+2.8
	Biradical formation reactions (Refs.30,32)	
25	$CH_4 \rightarrow H_2 + CH_2$	83.9
26	$-CH_3 \rightarrow H_2 + -CH$	78.7
27	$>CH_2 \rightarrow H_2 + \diagup\!\!>C$	73.5
28	$CH_3CH_3 \rightarrow CH_4 + CH_2$	68.4
29	$CH_3CH_2- \rightarrow CH_3 + CH_2$	71.0
30	$CH_3CH\diagup \rightarrow CH_2\diagup + CH_2$	73.6
31	$CH_3C\diagup\!\!\diagup \rightarrow CH\diagup\!\!\diagup + CH_2$	76.2
32	$-CH_2CH_3 \rightarrow CH_4 + -CH$	65.8
33	$>CHCH_3 \rightarrow CH_4 + \diagup\!\!>C$	63.2
34	$CH_3=CH_2 \rightarrow CH_3-CH$	45.9
35	$CH_2=CH- \rightarrow CH_3-C-$	43.3
36	$-CH=CH_2 \rightarrow -CH_2-CH$	48.5
37	$>C=CH_2 \rightarrow >CH-CH$	51.1
38	$CH\equiv CH \rightarrow CH_2=C$	65.5

When a hydrogen atom reacts with a molecule in which the reacting carbon atom is held by saturated σ bonds (reactions 19–22 of Table 3), the heat change (Q_5) is

$$Q_5 = E_{C-H} - 2\Delta H_H + E_{sp^3} - E_{sp^2} + m(2a - 1) \quad (11)$$

c. Biradical Formation Reactions

Table 3 includes the heats of some biradical formation reactions, which may be involved in the intermediate steps of a number of processes[46-52]. The active carbon atom in the biradical is assumed to be in the bivalent ground state with p^2 hybridisation of the orbitals. The heat (Q_6) of formation of such a biradical by the removal of a hydrogen molecule from the saturated hydrocarbon (reactions 25–27 of Table 3) is given by the expression

$$Q_6 = \Delta H_{C'} - E_{p^2} - \Delta H_C + E_{sp^3} - 2\Delta H_H + 2E_{C-H} + 4m(a-1). \quad (12)$$

The heats of the other reactions listed in Table 3 may be obtained in a similar way. The ability to calculate the heats of even hypothetical reactions is a useful feature of Eqn. (1), since it enables us to select the correct mechanism of various processes.

5. HALOGEN DERIVATIVES OF HYDROCARBONS

The ideas discussed above can be extended to halogen derivatives of hydrocarbons[25,29]. In this case, the contributions to the heat of formation of the gaseous halogenated hydrocarbon molecules and radicals of composition $C_nH_pX_v$ are given by the expression

$$\Delta H_{C_nH_pX_v} = n_1\Delta H_{C'} + (n-n_1)\,\Delta H_C + p\Delta H_H + v\Delta H_X - pE_{C-H} - vE_{C-X} - wE_{p^2} - fE_{sp^3} - gE_{sp^3} - hE_{sp} - sE_{C-C} - tE_{C=C} - uE_{C\equiv C} - m\sum_{i=1}^{n}(a+dk)\left(a+dk\frac{l_{CH}}{l_{CX}}\right), \quad (13)$$

where E_{C-X} is the energy of the covalent C–X bond, d is the number of halogen atoms on the i-th carbon atom, k is the proportionality coefficient[25] between the charge on the halogen atom and the charge on the hydrogen atom, l_{CH} and l_{CX} are the mean lengths of the CH and CX bonds.

Table 4. Characteristics of hydrogen and halogen atoms in hydrocarbons and their derivatives.

X	k	E_{C-X}, kcal mole^{-1}	l_{C-X}, Å (Ref.34)
H	1	78.71	1.09
F	−0.54	98.52	1.35
Cl	+0.27	63.89	1.75
Br	+0.43	50.47	1.93
I	+0.68	34.06	2.12

For the case of gaseous halogenated hydrocarbons of composition $C_nH_pX_v$ without conjugated double bonds, Eqn. (14) can be obtained from Eqn. (13) by transformations similar to those used in the derivation of Eqn. (2):

$$\Delta H_{C_nH_pX_v} = s\Delta H_{C_nH_4} + (f-2s)\,\Delta H_{CH_4} + t\Delta H_{C_nH_4} + u\Delta H_{C_nH_2} + v\,(\Delta H_X - \Delta H_H + E_{C-H} - E_{C-X}) + m\left[16f - 14s + 8t + 2u - \sum_{i=1}^{n}(a+dk)\left(a+dk\frac{l_{CH}}{l_{CX}}\right)\right]. \quad (14)$$

The quantities E_{C-X} and k are evaluated[25] by substituting into Eqn. (14) the known values of $\Delta H C_nHpX_v$ [33,34] listed in Table 4.

The following expression for the heat (Q_7) of removal of a halogen atom from halogenated alkanes (reactions 1–10 of Table 5) is readily obtained by using Hess's law and Eqn. (13):

$$Q_7 = E_{C-X} + E_{sp^3} - E_{sp^2} + m\left[ak\left(1+\frac{l_{CH}}{l_{CX}}\right) + (2d-1)\,k^2\frac{l_{CH}}{l_{CX}}\right]. \quad (15)$$

The heat of formation of biradicals from halogenated methane molecules by dehydrohalogenation (reactions 15, 17, 19 of Table 5) is given by the equation

$$Q_8 = \Delta H_{C'} - E_{p^2} - \Delta H_C + E_{sp^3} + \Delta H_{HX} - \Delta H_H - \Delta H_X + E_{C-H} + E_{C-X} - m\left[2a - 1 + (a+d-1)\,k\left(1+\frac{l_{CH}}{l_{CX}}\right) + (2d-1)\,k^2\frac{l_{CH}}{l_{CX}}\right] \quad (16)$$

where ΔH_{HX} is the heat of formation of a molecule of HX from its elements.

Table 5. Heats of formation of radicals from halogenated hydrocarbons.

No.	Reaction	X = F		X = Cl		X = Br		X = I	
		calc.	publ.	calc.	publ.	calc.	publ.	calc.	publ.
1	$CH_3X \rightarrow CH_3+X$	108.8	107[53]	79.4	78[53]	67.0	66.6[53]	52.1	52.6±±2.3[41]
2	$CH_2X_2 \rightarrow CH_2X+X$	110.6	109.6[52]	78.9	77.9[53]	66.3	65.5[53]	51.4	—
3	$CHX_3 \rightarrow CHX_2+X$	112.5	114.6[53]	78.5	78.3[53]	65.7	66.1[53]	50.6	—
4	$CX_4 \rightarrow CX_3+X$	114.4	116[53]	78.0	78.2[53]	65.1	66.6[53]	49.9	—
5	$-CH_2X \rightarrow -CH_2'+X$	110.0	—	78.8	83±7[54]; 77[55]	66.1	65.0[54]	50.8	51[41]
6	$-CHX_2 \rightarrow -CHX+X$	111.9	—	78.4	—	65.5	—	50.0	—
7	$-CX_3 \rightarrow -CX_2+X$	113.8	114[53]	77.9	—	64.9	—	49.3	—
8	$>CHX \rightarrow >CH+X$	111.3	—	78.2	73.3±2.3[41]	65.2	59[56]	49.4	52; 46[41]
9	$>CX_2 \rightarrow >CX+X$	113.2	109[53]	77.8	—	64.6	—	48.7	—
10	$>CX \rightarrow >C+X$	112.6	107[53]	77.7	75[55]	64.3	—	48.1	47[41]
11	$=CHX \rightarrow =CH+X$	124.6	—	91.6	85.5[54]	78.5	73.4[54]	62.8	66.5±2[41]
12	$=CX_2 \rightarrow =CX+X$	126.5	—	91.1	—	77.9	63±2[41]	62.0	—
13	$=CX \rightarrow =C+X$	125.9	—	91.0	—	77.7	—	61.4	—
14	$CH_3X \rightarrow H_2+CHX$	76.2	—	79.8	—	80.4	—	81.4	—
15	$CH_3X \rightarrow HX+CH_2$	60.8	—	62.8	—	66.1	—	63.7	—
16	$CH_2X_2 \rightarrow H_2+CX_2$	68.5	65.8*	75.8	—	77.0	—	78.9	—
17	$CH_2X_2 \rightarrow HX+CHX$	58.8	—	60.3	—	63.7	—	65.3	—
18	$CH_2X_2 \rightarrow X_2+CH_2$	171.8	—	87.3	—	66.7	—	38.8	—
19	$CHX_3 \rightarrow HX+CX_2$	56.8	58.4[58]	57.9	—	61.4	—	63.4	—
20	$CHX_3 \rightarrow X_2+CHX$	175.5	—	86.4	—	65.5	—	37.4	—
21	$CX_4 \rightarrow X_2+CX_2$	179.2	180.3*	85.5	—	64.3	—	36.0	—

* Values used in the calculations: ΔH_{CF_2} = −39.7 kcal mole^{-1} [57], $\Delta H_{CH_2F_2}$ = −105.5 kcal mole^{-1} [33], ΔH_{CF_4} = −220.0 kcal mole^{-1} [27].

The heats of the other reactions listed in Table 5 can be obtained by means of expressions derived in a similar way.

It is evident from Table 5 that the biradical mechanism, involving removal of a molecule of hydrogen fluoride, is energetically more favourable than the formation of monoradicals by removal of a fluorine atom in the thermal decomposition of fluorinated methane derivatives. The biradical mechanism was confirmed experimentally in the pyrolysis of methyl fluoride[59] and trifluoromethane[58,60]. A similar mechanism also applies to the decomposition of chloroalkanes with removal of an HCl

molecule[61-64]. Furthermore, the heats of formation of mono- and biradicals from bromo derivatives are very similar, suggesting that the two processes can occur in parallel[65,66], whereas with the iodo derivatives the mechanism involving breaking a C–I bond or the removal of an I_2 molecule is energetically more favourable. The decomposition of methyl or ethyl iodide is a well known method of producing alkyl monoradicals[67,68].

6. DISCUSSION OF SOME REACTIONS IN THE LIGHT OF THE PROPOSED APPROACH

A knowledge of the contributions to the heat of formation of hydrocarbons allows us to re-examine the mechanism of a number of reactions, and also to speculate on the nature of the activation energy attending various processes[30-32].

Table 6. Activation energies of some radical reactions involving hydrogen atom exchange*.

No.	Reaction	E, kcal mole^{-1} calc.	E, kcal mole^{-1} publ.	References
		Eqn.(17)		
1	$CH_3+CH_4\rightarrow CH_4+CH_3$	13.7	11.2–14.3	39, 43, 69–72
2	$CH_3+H_3C- \rightarrow CH_4+H_2C-$	11.1	9.3–10.4	39, 70–72
3	$CH_3+H_2C<\rightarrow CH_4+CH<$	8.5	8.0–8.7	39, 70–72
4	$CH_3+HC\equiv\rightarrow CH_4+C\equiv$	6.0	6.9–7.9	39, 70–72
5	$-CH_2+CH_4\rightarrow -CH_3+CH_3$	16.3	15.0–18	70,73
6	$-CH_2+H_3C-\rightarrow -CH_3+H_2C-$	13.7	13.9–16.9	70
7	$-CH_2+H_2C<\rightarrow -CH_3+CH<$	11.1	12.7–15.4	70
8	$-CH_2+HC\equiv\rightarrow -CH_3+C\equiv$	8.5	8.9–14.2	70,74
9	$>CH+CH_4\rightarrow >CH_2+CH_3$	18.9	18.7–20.2	70
10	$\equiv C+CH_4\rightarrow \equiv CH+CH_3$	21.4	22.7	70
11	$H+CH_4\rightarrow H_2+CH_3$	11.0	10.6±1.0	75
12	$H+H_3C-\rightarrow H_2+H_2C-$	8.4	9.5±2.0	75
13	$H+H_2C<\rightarrow H_2+HC<$	5.8	7.2±2.0	75
14	$H+HC\equiv\rightarrow H_2+C\equiv$	3.2	6.7±2.0	75
15	$H+H_2\rightarrow H_2+H$	—	6.2±1 7.5±1 7.3	39 43 76
		Eqn.(17a)		
16	$CH_3+H_2\rightarrow CH_4+H$	10.0	10.0	71,72
17	$-CH_2+H_2\rightarrow -CH_3+H$	12.6	13.3 12.2	72 73
18	$>CH+H_2\rightarrow >CH_2+H$	15.2	—	
19	$\equiv C+H_2\rightarrow \equiv CH+H$	17.8	—	

* Q values are listed in Table 3.

Thus, we can assume that in hydrogen atom exchange radical reactions, in which the reacting carbon atom of the original molecule is in the sp^3 hybridisation and that of the original radical is in the sp^2 hybridisation, the necessary condition is conversion of the sp^3 hybridisation of the carbon atom of the molecule into the sp^2 form, which requires an expenditure of 13.7 kcal mole^{-1} of energy. But since the heat of the reaction is altered by the interaction of the molecule and the radical, the activation energy barrier (E) which the system must overcome is given by the sum of 13.7 kcal mole^{-1} and the heat of the reaction, i.e.

$$E = 13{,}7 + Q \ . \qquad (17)$$

If the activated state of the hydrocarbon molecules for reactions 11–14 of Table 6 is similar to that for reactions 1–10, the activation energy can be calculated in a similar way from formula (17).

Leaving aside the nature of the active state of the hydrogen molecule, it is reasonable to assume that the same state is involved in reactions 16–19 of Table 6 as in the reaction between a hydrogen molecule and a hydrogen atom, for which the activation (or excitation) energy of the hydrogen molecule is approximately[39,43,76] 7.3 kcal mole^{-1}. Hence, the activation energy of reactions 16 to 19 can be obtained from the expression

$$E \approx 7.3 + Q \qquad (17a)$$

Reactions 2, 3, 4 of Table 6 differ from 5, 9, 10, and reactions 11–14 differ from 16–19, in being the reverse of the other process. The intermediate state of the system must be different in the two cases, as the difference between the activation energies for the forward and the reverse reaction is not equal to the heat of the reaction[31].

It is interesting to compare the activation energies for the cracking reactions of various saturated hydrocarbons with the heats of formation of the hydrocarbons from their biradicals. Thus, a biradical is formed from a methane molecule by reaction 25 of Table 3 with a heat absorption of 83.9 kcal mole^{-1}, and the activation energy for the cracking of methane is variously given[77,78] as 79–90 kcal mole^{-1}. On cracking ethane, biradicals are formed by reactions 26 and 28 (Table 3) with absorption of 78.7 and 68.4 kcal mole^{-1} respectively. The experimental values of the activation energy for this process lie in the range 68.7–79.5 kcal mole^{-1} [78,79]. In the pyrolysis of trifluoromethane the activation energy corresponds to the heat of formation of the biradical CF_2 [58]. It is a plausible assumption that a biradical is formed by reaction 34 of Table 3, with a heat of 45.9 kcal mole^{-1}, as an intermediate in the gas-phase hydrogenation of ethylene. This value is close to the experimentally observed[80,81] activation energy of the process (43–44.8 kcal mole^{-1}).

Unless the numerical agreement between these quantities is fortuitous, it suggests some definite conclusions as to the origin of the activation energy of these reactions, and in particular it suggests the widespread occurrence of a biradical mechanism. A comparison of the properties of mono- and biradicals leads to the same conclusion. Thus, monoradicals can recombine only as a result of mutual collisions, not by collisions with molecules[39,43,72]. Biradicals can be studied both in addition reactions and following internal electronic rearrangements to give a double bond[82-84]. Recombination of monoradicals occurs with a negligibly small activation energy[39,43,72]. Presumably, the same is true of biradicals[82,83,85]. There is evidence[46,86,87] that chain reactions account for a very small fraction of the total number of alkane molecules decomposed in cracking reactions: this confirms the likelihood of a biradical mechanism in reactions of this type.

In conclusion, we shall consider specifically the reactions

$$CH{\equiv}CH \rightarrow CH{\equiv}C + H \qquad (18)$$

and

$$CH{\equiv}CH \rightarrow C{\equiv}C + 2\,H \ . \qquad (19)$$

Reaction (18) requires the expenditure of ~121 kcal mole^{-1} [39,88], and reaction (19) requires 246 kcal mole^{-1} [40]. Since the reacting quadrivalent carbon atom is converted from sp hybridisation to a valency state without any hybridisation of the orbitals, we can use the heats of these reactions to calculate the energy evolved as a result of sp hybridisation. The mean value of E_{sp} is ~42 kcal mole^{-1} (41 kcal mole^{-1} by reaction (18) and 43 kcal mole^{-1} by reaction (19)). Hence, according to Eqn. (6), the heat of formation of a quadrivalent carbon atom from graphite is approximately $\Delta H_C = 192$ kcal g-atom^{-1}. But since the heat of formation of gaseous carbon in the ground state is 171.7 kcal g-atom^{-1}, it follows that the transition of a $2s$ electron to a $2p$ orbital requires ~20 kcal g-atom^{-1}. Using the above value of ΔH_C and Eqns. (4) and (5), the energy evolved during sp^3 and sp^2 hybridisation can be calculated: $E_{sp^3} = 83$ kcal g-atom^{-1} and $E_{sp^2} = 69$ kcal g-atom^{-1}. Thus, the ideas discussed in this review allow quantitative evaluation of a number of important parameters in the chemistry of hydrocarbons.

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Complexing Adsorption Chromatography and Its Prospects

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Investigations on complexing adsorption chromatography during its period of existence (1954-1970) are reviewed, and possible ways for its future development are considered.
The method was developed originally for preparing the extremely pure salts used in the production of phosphors, and then grew to be a general method of separating substances, enabling the most selective processes to be accomplished by simple procedures. However, widespread introduction of the method is hindered by the absence of published summaries covering technique, theory, and fields of application. The present review covers these aspects, and will enable research workers to apply the method correctly and to extend its field of use in the laboratory and in industry. A list of 80 references is included.

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I. INTRODUCTION

The problem of the selective extraction of substances from complicated mixtures has recently become especially important, as a consequence of the development of many branches of chemistry and technology which require the use of pure and ultrapure materials. Establishment of the most effective and economical methods for isolating, separating, and purifying substances is necessary to meet the demands of the development of nuclear energy, the manufacture of semiconductors, phosphors, and single crystals, the rational exploitation of combined ores, and many other branches of industry and fields of science.

Chromatography has played a considerable part in solving these problems, enabling pure substances to be obtained in various areas of chemical science and industry, including the selective extraction of substances from complicated mixtures.

The greatest difficulties arise in the development of procedures for obtaining pure and ultrapure materials and separating elements of closely similar properties. The practical solution of this problem requires the use of especially delicate and effective methods, since the usual chromatographic methods, based on the use of general-purpose sorbents (including ion exchangers), often prove ineffective. In this connection research workers have recently directed their efforts towards producing selective sorbents characterised not only by group but also by individual specificity towards particular elements. The development of such sorbents is extremely promising, since their practical use will enable the best separation to be obtained. Efforts to obtain such sorbents have been made for a long time, a particularly large number of papers having been published during recent years (see the reviews[1-3]).

It is well known that ordinary general-purpose ion exchangers possess some measure of selectivity, which is responsible for the sequential sorption of ions in so called "adsorption series". Selective exchangers, however, exhibit a more clearly pronounced selectivity, as a consequence of the presence in the polymer matrix of specific active groups, most often complex-forming.

General-purpose exchangers also often exhibit complexing properties, leading to a decrease in the degree of dissociation of ionogenic groups and hence an increase in selectivity. For example, cation-exchange resins containing carboxylate and phosphate groups, and also anion-exchange resins of low and medium basicity, absorb metal ions as a result of complex formation. Specially prepared selective exchangers usually contain ionogenic groups capable of forming inner complexes with metal cations. They are prepared by introducing an appropriate chelating agent into the polymer matrix. However, existing methods do not yet allow us to obtain selective exchangers having specified properties or with any active group, in spite of the varied range of specific reagents available to the modern analytical chemist. This explains the hitherto insignificant use which selective exchangers have found[1-10].

However, other opportunities for highly selective chromatographic separations can be realised by creating special conditions under which a rich variety of specific reagents of different kinds can be used for these processes.

The origin of this line of development was the use of precipitation chromatography[11-14] for many complicated separations by the simplest procedures. An almost unlimited number of chemical reagents can be used as precipitants in the columns. However, the broadest opportunities for selective separations are to be expected from the application of complexing agents by the method of complexing adsorption chromatography[15-20]. A great part in establishing this method and working out its physicochemical principles was played by Gurvich[15-20].

In contrast to precipitation chromatography, in which an inert support is used and the precipitates are frequently not attached to the carrier, but more along the column with the stream of solution, complexing adsorption chromatography uses as carrier a sorbent capable of retaining both the complexing agent and the products of its reaction with metal cations, which vary in solubility.

The complexing adsorption column consists of a sorbent carrier, which retains the complexing reagent sorbed on its surface. The term "modified" has recently been applied to such sorbents. When the solution of a mixture of substances is filtered through the column, separation occurs as a consequence of the differences in their capacity

for complex formation with the given reagent, in the stability of the complexes which are formed, and also in their sorbability on the given sorbent carrier. Separation is intensified also by the chromatographic method itself, a distinguishing feature of which is a multiplicity of elementary acts of separation. The reaction products are retained on the sorbent carrier in the column as sparingly soluble complex compounds (sometimes as soluble complexes). At the same time substances which do not react with the given complexing agent pass freely through the column into the filtrate.

Thus a selective process of separation can be realised most fully in the complexing adsorption method, the main factor in the present case being the selectivity of the complexing agent. Advances in the preparation of a large variety of such reagents opens up wide prospects for developing the method and extending its fields of application. Successful separation requires that the appropriate complexing agent and carrier should be matched, the properties of the modified sorbent studied, and also optimum conditions chosen. The conditions of separation include the most varied procedures used in chromatography—use of particular masking complexing agents, variation in solution pH, temperature, and rate of filtration—together with other procedures which may in some measure enhance the specificity of the reagent and the selectivity of the method. By this means columns possessing exceptional selectivity can be prepared by simple procedures using ordinary chemical reagents together with cheap and readily available sorbents.

The separation of substances by complexing adsorption chromatography is accomplished in several cases with only one filtration of the mixture through the column, whereas even complexing elution requires two stages—production of the primary chromatogram, followed by displacement by the eluent.

The procedures of complexing adsorption chromatography closely resemble those of precipitation chromatography, from which the method arose historically as a consequence of improving the latter by replacing the inert carrier by a sorbent actively involved in the process of separation[18]. The method was originally termed "adsorption–precipitation chromatography", but since in most cases sorbable reagents were used, which formed complexes with the separable substances, also sorbed to some extent on the carrier, the term "complexing adsorption chromatographic method" was adopted later[17,18].

Adsorption phenomena are secondary in precipitation chromatography; they always accompany separation to some extent. In the complexing adsorption method, however, adsorption phenomena are a factor determining the possibility of separation[19].

Since substances are more easily adsorbed from a given solvent the less soluble they are in it, the present method is applied most frequently to the separation of substances which react with the reagent to form products of limited solubility. It is interesting that sometimes, where several reactions are possible between a given substance and the complexing agent, reaction which leads to the formation of the most easily adsorbed product is accelerated under the conditions of a column. In this connection complex formation quite often involves different reaction mechanisms under static conditions and in the column[18,19]. Precipitation chromatography can be regarded as the limiting case of the adsorption—precipitation method in which, in view of the sparing solubility and the "tenacity" of all the compounds formed in the column, the adsorbent can be replaced by an inert support.

II. PHYSICOCHEMICAL PRINCIPLES OF COMPLEXING ADSORPTION CHROMATOGRAPHY

Detailed investigation of the processes accompanying the complexing adsorption of metals has revealed several specific features of this method[19]. It is distinguished from other methods of chromatographic analysis mainly by the conditions of application of complex formation, a reaction which is widely used for the separation of substances in both static and dynamic processes. Opportunities for the application of complex formation were especially broadened by the development of chromatography. Complexing processes became an important factor in separation both in ion-exchange and adsorption and in partition and precipitation chromatography.

The method of applying complexing agents most widely used in classical adsorption chromatography is development of the primary chromatogram. In this case the developer reacts with already separated substances, without taking part in their separation. Metals can be separated also by chromatographing mixtures of their soluble complexes on molecular sorbents, e.g. on aluminium oxide[21–23].

In ion-exchange chromatography a very widely used method for developing the primary chromatogram of the ions is the use of solutions of organic reagents which form readily soluble complexes with the separable cations. This procedure is especially valuable for the separation of rare-earth elements[24]. An analogous method is employed in partition chromatography[25]. In some cases the use of ion-exchange columns to separate complex ions obtained in solution or to segregate them from other substances is effective[26,27].

In isolated cases precipitation chromatography also makes use of sparingly soluble complexing agents in the form of chemisorbents together with carriers which are inert towards reactants and reaction products[11,27]. The fundamental process in precipitation chromatography is the formation of sparingly soluble compounds as a new phase, while adsorption processes, as already stated above, are secondary and may exert different and opposite effects on the separation.

In the method under review complex formation is invariably combined with sorption processes: no new solid phase is formed. The complexing agent is first attached to the sorbent carrier by sorption interaction, and then a solution of the mixture is introduced into the column. Separation in such a column is determined by the difference in the instability constants of the complexes formed by the cations with the complexing agent, these latter also being in some measure retained on the sorbent carrier by sorption forces. Under the most favourable conditions for separation some elements form complexes and are attached to the column, while others do not form such compounds and pass into the filtrate. One of the components can then be isolated in pure form, as has been achieved, for instance, in the thorough purification of salts used in the production of phosphors [15,16,19]. Thus in this method the possibility of separation is governed by the sorption interaction of the complexes with the sorbent carrier.

In this connection it is important to note also that, in the limiting case, the formation of sparingly soluble complexes takes place in the complexing adsorption method without isolation of a new solid phase: they are attached by van der Waals forces to the surface of the sorbent carrier at the instant of their formation, i.e. bypassing the precipitation stage, apparently becuase the bonding between

molecules of the complex and the surface of the sorbent is stronger than that between molecules of the complex in its crystals. It should be noted that the complexes which are formed may vary in solubility.

One condition for use of the complexing elution of chromatographic columns is that the reagent should be more or less soluble. This is a second stage, following formation of the primary chromatogram, and the ion forming the most stable compound is the first to pass into the filtrate. In contrast to this, the condition for application of the complexing adsorption method is that the reagent should be relatively sparingly soluble but readily adsorbed on the sorbent carrier, so that the reagent remains in the column and does not contaminate the solution of separable cations. Separation is accomplished by the application of only one process—filtration of the solution of separable substances through the column—and the cation forming the least stable complex is the first to pass through into the filtrate. This fact is responsible for the high selectivity of complexing adsorption columns and the possibility of using them to purify large quantities of substances, which do not react with the complexing agent, from impurities which form with the latter complex compounds that are sorbed on the carrier.

It is an extraordinarily complicated task to reveal the main laws and the mechanism of complexing adsorption, especially in view of the multiplicity of combinations in the preparation of modified sorbents, where both the properties of the carrier itself and of the complexing agent and also qualitatively new characteristics of the modified sorbent and those of the separable system may develop and influence the process.

One of the most important factors determining the mechanism of complexing adsorption is the nature of the sorbent carrier. The demands made on the latter by the essential nature of the method reduce basically to the following: the carrier should be insoluble in water or other solvent and possess a sufficiently large surface, the ability to sorb molecularly the complexing agents and their reaction products with the separable substances, good filtering ability, mechanical and chemical stability, and optimum kinetic characteristics. Existing sorbents may only partly satisfy these main requirements.

If the sorbent carrier contains any soluble components, they may be extracted during the process and further contaminate the solution of separable substances. The sorbents sometimes contain soluble components and mineral impurities, which are easily removed by careful preliminary washing.

The advisability of using a particular sorbent carrier depends in large measure on its adsorption capacity. In this connection sorbents having a maximum surface area, because of the presence either of pores or of a network structure, should be preferred. It is important that molecules of the modifier (i.e. of the already sorbed complexing agent) should be accessible for subsequent reaction with the separable ions.

The main type of sorption in the present method would be molecular sorption on to the carriers both of the complexing agents and of the metal complexes formed in the process of separation. Most sorbents contain various functional groups and energetically non-uniform centres, and one mechanism or another may predominate depending on the conditions of sorption. A study of the mechanism of sorption is therefore of great value in choosing the most suitable carrier–modifier system for a particular process.

The good filtering power, mechanical durability, and chemical resistance demanded of a sorbent carrier are governed by its operating conditions. Filtering power depends on the grain size of the sorbent, which is selected within optimum limits for a given size of column and a given rate of filtration of the solution. Adequate mechanical durability of the sorbent is important on prolonged operations, especially if it is desirable to regenerate the sorbent and use it many times. Various corrosive media may be employed during separation or sorbent regeneration, so that the chemical resistance of the sorbent is also quite important. Changes in the sorbent resulting from chemical reactions may lead not only to contamination of the solution but also to mechanical disintegration and loss of sorption capacity.

Modifying the surface of a sorbent carrier by the sorption of various complexing agents yields a qualitatively new sorbent: not only the chemical but also the physical properties of its surface have changed. The pore size and hence the total surface vary depending on the quantity of complexing agent sorbed by the carrier. The absorption of metal ions takes place on a modified sorbent, as a consequence of their chemical reaction with the complexing agent and the formation of new complexes. Other types of sorption, characteristic of the unmodified carrier, may be either partly or completely suppressed.

It must be borne in mind that the chemical reactions occurring in a complexing adsorption column may differ from those in solution[19]. For example, compounds which are unstable in solution under ordinary conditions are often formed in a column and exist for a long time[12–14]; in other cases certain reactions, which are not feasible under static conditions, may go to completion in a column[19]. These aspects of the accomplishment of reactions directly in columns may find the widest practical application, from the separation of different modifications of chemical compounds to reactions which occur with difficulty under static conditions, including catalytic processes for organic and for inorganic substances.

We have investigated the mechanism of the sorption of complexing agents and inorganic ions on active carbon[28,29], and shown that the former (e.g. dimethylglyoxime, 1-nitroso-2-naphthol, 8-hydroxyquinoline, tannin, xanthates, dithizone, diethyldithiocarbamates, derivatives of hydroxamic acids, phenylarsonic acid, thionalide, thiourea, etc.) undergo sorption of molecular type. Carbon is able to retain firmly 10–20% of the complexing agent, about 1.0–3.0 mg-equiv.g^{-1}, while the ion-exchange sorption of inorganic ions on active carbon is only 0.05 to 0.07 mg-equiv.g^{-1}. These results are consistent with those obtained by other workers[19,30]. It was established also that the sorption of the complexes formed with metal ions is molecular in character[28,29].

The fact that sorption can occur on active carbon by two mechanisms—molecular and ion-exchange—does not prevent its use as a carrier in the complexing adsorption method. Ion-exchange sorption has been shown[28,29] to predominate at low (up to 1%) surface coverage by the modifier. Above 1% coverage this is suppressed by sorption of the complexing agent, and the metal is absorbed by the complexing adsorption mechanism. We can therefore regard modified active carbon as monofunctional, corresponding in its action to the complexing modifier sorbed on it.

The optimum quantity of modifier on the carrier should be found empirically in each individual case. The total absorption capacity of the metal increases with increase in the coverage of carbon by the modifier[28,29], while the degree of utilisation of the complexing agent diminishes. However, the most complete exploitation of the modifier,

in some cases even ~100%, can be attained by selecting experimental conditions under which the metal ion is complexed to the maximum extent. This is usually achieved by choosing the optimum pH for the given system[22,28,29].

The temperature conditions are very important for separations by the complexing adsorption method. Rise in temperature tends to increase the rate of absorption of a metal cation. A considerable temperature effect can be used for intensifying complexing adsorption, since it tends to increase the productivity of the columns and permits higher rates of filtration.

All the above factors, influencing in some measure the separation of substances by complexing adsorption, must obviously be taken into account in determining optimum procedures for the chromatographic processes.

III. CONDITIONS OF APPLICATION OF SORBENT CARRIERS AND COMPLEXING AGENTS IN COMPLEXING ADSORPTION CHROMATOGRAPHY

Very few sorbent carriers at present available for complexing adsorption satisfy the above requirements. The most widely used for these purposes is active carbon, which was first employed by the originators of this method[15,17]. Subsequently technical conditions were developed for "active wood charcoal for chromatography" (DAUKh) [19], which was used in industry for obtaining high-purity salts employed in the manufacture of phosphors. In contrast to other carriers, charcoal, like most carbon sorbents, is a readily available and cheap material, possessing adequate sorption capacity, mechanical and thermal durability, and structural stability. The oblong grains of DAUKh charcoal have a cross-section of 0.2–0.6 mm. Carbon of such grain-size ensures a satisfactory rate of filtration when used in fairly large columns[19]. Complexing adsorption processes have been accomplished also on other brands of carbon[31–35].

Other sorbents, e.g. Wofatit E[36], whose capacity is several times greater than that of active carbon, have been used as carriers. Our investigations indicate that Wofatit E is useful as a sorbent carrier in processes where strong selective absorption is required. This resin is unsuitable for very fine separations, since with strong absorption substances of similar properties exhibit no differences in behaviour.

Among Soviet synthetic materials it is only recently that macroporous resins have been synthesised which are capable of both molecular and ion-exchange sorption. Such resins may be supposed to be good sorbent carriers for complexing agents.

Experience in the application of various complexing agents has enabled us to recommend several general and special procedures for modifying carbon in order to prepare selective sorbents. Charcoal can conveniently be freed from mineral impurities by pretreatment with 5–10% hydrochloric (or sulphuric) acid heated to 60–70°C.[16] The completeness of extraction of mineral impurities—mainly iron, copper, and potassium—must be checked by application of the most sensitive analytical methods to the filtrate. After treatment the excess acid must be washed out of the charcoal with distilled water until the washings are neutral to Methyl Orange, and the carbon brought to an air-dry state.

The method used to prepare the modified carbon may vary with the properties of the complexing agent. Sorption of sparingly soluble, non-volatile reagents (e.g. dimethylglyoxime, *N*-hydroxy-*N*-phenylbenzamide) is best accomplished by heating an aqueous suspension with carbon on a water-bath at 70°C. Heating is advisable to accelerate dissolution of the reagent and to remove air. As reagent is absorbed, fresh portions gradually dissolve and pass into the sorbed state. Soluble reagents (e.g. diethyldithiocarbamate, tannin, phenylarsonic acid) may be sorbed from aqueous suspension on shaking. It is advisable to preheat the suspension at 70°C for 5–10 min to remove air bubbles. Heating is inadvisable for the sorption of reagents which are volatile in steam (e.g. hydroxyquinoline). In this case saturation must be accomplished at ordinary temperatures, by shaking an aqueous suspension of carbon with the reagent. It is advisable to preheat an aqueous suspension of the carbon (without the reagent) at 70°C, and then cool it. Completion of sorption is assessed by disappearance of the corresponding colour from the solution when a sensitive qualitative test is applied for the given reagent.

The quantity of complexing reagent which can be retained in the sorbed state on DAUKh charcoal is usually 10–20% based on the weight of carbon.

Most complexing agents are firmly sorbed on the carbon surface, and hardly any desorption occurs on washing with water or on the passage of considerable volumes of solution. But in some cases, e.g. in the sorption of tannin, the reagent is not firmly retained on the carbon surface, and is gradually washed out of the column. In order to secure better attachment of such reagents, it is advisable after sorption to dry the modified carbon without washing it with water[29,37].

Some sorbents absorb well from solutions in organic solvents, e.g. dithizone from chloroform solution on to carbon[31]. The modified sorbent obtained sorbs heavy metals well from aqueous solutions.

An interesting method is to impregnate active carbons and other inert carriers with liquid organic reagents. McClaine and Noble[32,33] extracted uranium selectively on carbon treated with organophosphorus acid derivatives, which give stable chelate complexes with several metals, in particular uranium. Such sorbents have been employed in industry to extract rare metals.

In some cases a modifier is deposited from the vapour phase on to a carrier[38,39]. A carbon–titanium sorbent, which absorbs uranium selectively, has been obtained in this way.

The application of modified sorbents under dynamic conditions—in complexing adsorption chromatographic columns—is most effective, and we shall be concerned here mainly with this method.

Independently of column size (from laboratory to industrial dimensions) the modified sorbent is introduced as a suspension in an appropriate solvent (aqueous suspensions are mostly used). If the modified sorbent required is in a dry form, its aqueous suspension is first heated at 70°C. This is especially important in cases in which separation is effected at high temperatures, since dissolved air would be evolved from an unheated suspension, and might cause swelling of the sorbent layer.

If substances which do not react with the modifier are to be thoroughly freed from impurities that react with it to form stable sorbable compounds, it is advisable to place a layer of the pure sorbent carrier below the layer of modified sorbent, in order to prevent contamination of the filtrate with compounds that may be partly desorbed from the modified sorbent layer. The pure carrier is introduced into the column by the same procedures as the modified sorbent.

In the preparation of modified sorbents it must be borne in mind that the reactions of complexing agents on sorbent carriers with metal ions often occur differently from in a homogeneous medium. The special features of the process are exploited to intensify the separation effect (e.g. with dimethylglyoxime, 1-nitro-2-naphthol, xanthates, etc.). Sometimes, however, reactions in columns do not produce the expected separation, owing to the occurrence of undesired reactions.

An example of the complicating effect of the sorbent carrier is provided by columns containing carbon modified with sodium tetraphenylborate, a selective reagent for precipitation of the univalent ions K^+, Rb^+, Cs^+, NH_4^+, Ag^+, Hg_2^{2+}, and Tl^+. The solubility products of compounds of these metals with tetraphenylborate lie in the range 2×10^{-8}–5×10^{-10}. It would therefore appear promising to use such columns for the selective absorption of these ions from solutions of salts of other metals, especially for the thorough purification of sodium salts. However, our investigations of the sorption of potassium from aqueous salt solutions has revealed certain anomalies in this process. Potassium is completely absorbed on a carbon–tetraphenylborate column provided that sodium is absent from the solution: in the presence of sodium salts, however, the sorption of potassium is considerably weaker. Potassium absorbed by a column is displaced by sodium salts. A precipitate of potassium tetraphenylborate obtained in the absence of carbon is decomposed on addition of the latter to the system, with the liberation of K^+ and BO_3^{3-} ions. We explain this by the following decomposition of tetraphenylborate in the presence of carbon

$$(C_6H_5)_4BK + 4H_2O \rightleftarrows H_3BO_3 + KOH + 4C_6H_6 . \quad (1)$$

The decomposition of sodium tetraphenylborate occurs according to the equation[40]

$$(C_6H_5)_4BNa + 3H_2O \rightleftarrows C_6H_5B(OH)_2 + 3C_6H_6 + NaOH . \quad (2)$$

Detection of the BO_3^{3-} ion in solution indicates that reaction (1) takes place in the presence of carbon. It is interesting that displacement of the reaction to the right-hand side, i.e. liberation of the K^+ ion, does not take place from a precipitate of potassium tetraphenylborate in sodium iodide solution. Carbon evidently catalyses the decomposition of tetraphenylborate. For this reason sodium salts cannot be completely freed from contamination by potassium using a carbon–tetraphenylborate column. The maximum degree of purification achievable by this method does not exceed 0.0016%.

In some cases the sorption capacity is diminished when a sorbent is modified, owing to blocking of the active groups of the modifier. An example is provided by Dzhelassi and Egorov[41], who investigated the sorption of germanium on BAU carbon, alumina, and EDE-10P anion exchanger, all treated with dimethylaminophenylfluorone. It was found that after such treatment the sorption of germanium increased on the anion exchanger, but diminished on carbon and on alumina. The explanation offered[41] was that, when the modifier is sorbed on carbon and alumina, the *ortho*-dihydroxy-groups capable of reacting with germanium lose their activity.

The above examples show that a favourable effect cannot always be expected after modification of a sorbent. When the expected effect is not achieved, the reasons must be ascertained, and if possible another modifier–carrier system chosen.

Experience in the application of several complexing agents has shown that most selective isolations can be conducted more efficiently in complexing adsorption columns than in solution. The development of the theory of complex formation during recent years has revealed new opportunities for accomplishing many specific separations which can be successfully used in the complexing adsorption method. Complexes of the chelate type—hydroxyquinoline, dithizone, *N*-hydroxy-*N*-phenylbenzamide, diethyldithiocarbamate, pyridylazoresorcinol, pyridylazonaphthol, dimethylglyoxime, etc.—should play a special part here. If masking agents are used, chelate compounds provide the widest possibilities for the isolation and separation of pure elements. The number of chelate compounds studied is continually increasing, with an accompanying increase in the possibility of choosing systems having the maximum selectivity for extracting rare, trace, and other impurity elements[80].

IV. FIELDS OF APPLICATION OF COMPLEXING ADSORPTION CHROMATOGRAPHY

1. Production of Pure Salts

Complexing adsorption chromatography was developed during 1954–1957 in solving purely manufacturing problems[15,16,19,28]. The first field of application of this method was the production of high-purity salts used in the manufacture of phosphors. This problem was successfully solved for the purpose of purifying metals, which do not react with the complexing agent in the column, from impurity metals which form stable and firmly adsorbed compounds with it (e.g. the purification of zinc and cadmium sulphates from traces of copper, iron, nickel, and cobalt)[16,19]. The columns used consisted of two layers: the lower layer contained active carbon; the upper layer comprised active carbon and a complexing agent (e.g. dimethylglyoxime or 1-nitroso-2-naphthol) to react with impurities, in the proportions 10 : 1. The purpose of the lower layer was to prevent the partly water-soluble organic reagent from breaking through into the filtrate. The complex compounds formed in the column were firmly retained on the surface of the carbon. Purification of dissolved salts of zinc, cadmium, alkali metals, and alkaline-earth metals in the presence of hydrogen peroxide at pH 5.8–7.2 on such carbon–dimethylglyoxime and carbon–1-nitroso-2-naphthol columns lowered the concentration of copper, iron, nickel, and cobalt to 1×10^{-9}–4×10^{-8} g ml^{-1}.[16,19,28]

The fact that in this case the complexing agent does not react with the cations of the salts to be purified is responsible for the selective sorption of impurities by the columns, the lack of an effect of the initial impurity concentration on the degree of purification of the solutions (this can be assessed from colorimetric and luminescence analyses), and the extremely high operating capacity of such columns. In the purification of reagent salts with impurity contents exceeding the standard level by factors of 10–1000 the capacity of the column is measured in tons of solution for kilograms of sorbent. The use of carbon–dimethylglyoxime columns to purify the raw materials for the production of phosphors has been adopted by industry, and is applied successfully in both works and laboratory[15–18,20,42–44]. Carbon–*o*-hydroxyquinoline columns can be used to purify alkali-metal salts from heavy metals[15].

Cations which react with the complexing agent can also be separated by means of a complexing adsorption column. As in other applications of chromatography, it is important that there should be a sufficiently large difference in properties (stability constants of the complexes).

For example, a carbon–dimethylglyoxime column can be used to free cobalt salts from contamination by nickel[20]. Cobalt is the first to pass into the filtrate, as it forms a less stable compound with dimethylglyoxime in the column than does nickel. Chemical analysis does not detect nickel in the filtrate, and during purification the cobalt salt does not become contaminated with any substances which it did not contain before purification. In this case the lower layer of the column, which retains the cobalt dimethylglyoximine desorbed from the upper layer, should not be too small.

When the solutions to be purified contain cobalt, it is advisable to use carbon–1-nitroso-2-naphthol columns. These have some advantage over carbon–dimethylglyoxime columns, since they are able to free from cobalt more concentrated (20–25%) zinc sulphate solutions[17]. Furthermore, cobalt dimethylglyoximine begins to be desorbed relatively rapidly from the column, which is not observed when 1-nitroso-2-naphthol is used. In cases in which it is desirable to recover the absorbed nickel and cobalt, however, it is advisable to use dimethylglyoxime columns, since the reaction between dimethylglyoxime and metal cations is reversible in a column (unlike the reaction under static conditions), and the absorbed nickel and cobalt can be extracted with a small volume of aqueous hydrochloric acid[17].

Modified sorbents which bind the main substance but do not react with impurities can also be used to obtain high-purity products. We proposed a method of purifying radioactive niobium-95 from microquantities of antimony-125 on a carbon–*N*-hydroxy-*N*-phenylbenzamide column[29,44] from tartrate solutions buffered to pH 4.5–5.5 with ammoniacal ammonium acetate at 90°C. The column had first been washed with the same buffer mixture. The niobium complex of the modifier formed on filtration was retained in the column, whereas at this pH the antimony passed freely into the filtrate. The niobium sorbed in the column was then washed out with the buffer mixture at the same temperature. Analysis of the filtrates by means of a γ-ray spectrometer showed that the first portions of the filtrate contained the pure radioactive isotope ^{125}Sb, and subsequent fractions contained the pure radioactive isotope ^{95}Nb.

2. Group Separation or Isolation of One Component from a Mixture

The complexing adsorption method has recently become widely used for the separation of metals into groups and for the isolation of one component from a mixture. The application of modified sorbents is especially important when other methods prove ineffective (e.g. in the separation of rare-earth, rare, and trace elements).

We have recommended carbon–xanthate columns for the segregation of alkali and alkaline-earth metals from heavy metals and for the separation of metals which react with xanthates to form sparingly soluble compounds (e.g. Cu^{2+} from Zn^{2+}, Ni^{2+}, etc.)[43].

Conditions have been described for the separation and purification of metals by means of dithizone[31,43,45–47], sodium diethyldithiocarbamate[43,48], zinc and cadmium diethyldithiocarbamates[49], and several other complexing agents[50]. Aleksovskii[51,52] proposed a specially prepared zinc aluminosilicate as sorbent carrier for sodium diethyldithiocarbamate: after modification with a 1% solution of this salt a sorbent which is selective towards copper is obtained. Pierce and Peck[53] recommend that dithizone should be sorbed on acetylated cellulose, and the modified sorbent was used for the selective extraction of zinc, shown to be absorbed by the reaction $Zn^{2+} + 2HDz = ZnDz_2 + 2H^+$.

Hesford[54] recommends that active carbon should be saturated with bases—aqueous ammonia, methylamine, diethylamine, alkylamines, hexamines, pyridine, etc.—having different dissociation constants. Strong bases were used to segregate most cations, which form insoluble hydroxides, from alkali and alkaline-earth metals. Weak or complexing bases were used to isolate or separate certain cations.

Andreev et al.[31] applied the method for the selective isolation and concentration of lead, iron, copper, manganese, cobalt, and cadmium present in microconcentrations in natural waters. Active carbon of KAD and BAU brands was used as sorbent carrier. The dithizone modifier was sorbed from chloroform solution, and subsequently removed by the solvent. Carbon–dithizone columns containing an underlayer of pure carbon possess considerable capacity for the above elements, and are capable of multiple extraction and concentration of metals. The absorbed metals can be isolated into the filtrate with a small volume of weak hydrochloric acid, after which the column is ready for further use without additional regeneration.

3. Concentration of Metals

The complexing adsorption method makes it possible not only to isolate but also to concentrate metals from very dilute solutions ($\leq$ 0.2–0.3 mg litre^{-1}). The metal extracted by the column from a salt solution in which it occurred at a low concentration can be desorbed by decomposing the complex formed in the column and can be concentrated into a small volume of solution. For example, nickel can be segregated on a carbon–dimethylglyoxime column from excess of such a salt as zinc sulphate or sodium sulphate, and then extracted from the column with a small quantity of dilute hydrochloric acid; this increases the nickel concentration a hundredfold[17]. Similarly the reversibility of the reaction between cobalt and dimethylglyoxime in a column, in contrast to the reaction under static conditions, can be used to recover the cobalt removed in the purification of zinc sulphate solution.

4. Qualitative Analysis of Ions

The complexing adsorption method is no less effective for the qualitative analysis of mixtures of ions. Visual observation on colourless adsorbents is most suitable for this purpose. For example, aluminium oxide "for chromatography", after it has been wetted with water, is able to adsorb from aqueous solution metal complexes of dimethylglyoxime. The adsorption properties of aluminium oxide can be exploited by using water-saturated columns of the oxide mixed with dimethylglyoxime, e.g. in the proportions 10 : 1, for the qualitative determination of nickel and cobalt when present together[20]. In such a column nickel forms a pinkish-red zone, and cobalt forms a yellow zone below the nickel zone. It is possible in this way to detect 0.4 μg of nickel at a dilution of 250 000 : 1 in a 3700-fold excess of cobalt, and 2.9 μg cobalt at a dilution of 34 500 : 1 in a 500-fold excess of nickel. Mixtures of Co^{2+}, Ni^{2+}, and Fe^{2+} can also be separated on such columns[55].

The wide possibilities of combining various complexing agents with sorbent carriers has enabled a systematic qualitative analysis of ions to be based on this method[56,57]. It gives entirely reliable detection of micro-quantities of ions.

5. Study of Complex Formation under Dynamic Conditions

Gurvich showed the great possibilities of the method for investigating complex formation in a column[42,55]. Using as example a carbon–dimethylglyoxime column, he obtained new information on the properties of organic reagents, the structure and stability of their compounds with metals, the formation of compounds whose existence had not previously been detected, etc. Thus it has been established that in a carbon–dimethylglyoxime column bivalent nickel, cobalt, copper, and iron form compounds of general formula $M(HDm)_2$, and their relative stabilities have been determined. On such a column these cations form the sequence—$Cu^{2+} > Ni^{2+}$, $Co^{2+} > Fe^{2+}$—in order of diminishing sorbability. This coincides with the order of decreasing stability of their dimethylglyoximines of type $M(HDm)_2$. The order of diminishing stability—$Cu^{2+} > Ni^{2+} > Fe^{2+}$—has been found similarly for the 1-nitroso-2-naphtholates.

Study of the order of sorbability of Cu^{2+} and Fe^{3+} on a carbon–dimethylglyoxime column indicated[42] the existence of compounds—iron(III) copper dimethylglyoximines—in which dimethylglyoxime was combined with both metals. In fact, these compounds were subsequently detected when the reactions were conducted under static conditions. Iron(III) dimethylglyoximine was detected on a column formed by a mixture of aluminium oxide and dimethylglyoxime. This was later confirmed by conducting the reaction between an iron(III) salt and an aqueous solution of dimethylglyoxime under static conditions[55].

6. Extraction of Rare and Trace Elements

Complexing adsorption chromatography has a great future for the incidental extraction of rare and trace elements in the combined exploitation of ores. Appropriate choice of the sorbent carrier and also of the complexing agent will make it possible to extract completely valuable impurities present in minute quantities in the original raw material, and then to obtain them as concentrates. An example of such application is the industrial extraction of germanium from copper schists on columns of Wofatit E saturated with tannin[36]. Germanium was sorbed from 0.1 *N* sulphuric acid having a germanium content of 15 to 200 mg litre^{-1} and with a minimum ratio of germanium to the other elements in the lye of 1 : 10 000. Germanium was sorbed selectively, and the quantity remaining in the mixture did not exceed 0.1 mg litre^{-1}. It was desorbed by means of 9–10 *N* hydrochloric acid: the quantity of tannin thus extracted was so minute that only after 6–8 cycles did some diminution in the capacity of the column for germanium become appreciable. The amount of tannin required to regenerate the column was only 25% of the original quantity.

Other modified sorbents have been examined for the selective extraction of germanium[34,41,58–62]. Matveeva and Press[34] sorbed tannin on KAD–iodide carbon and on AN-1 anion exchanger. The sorption of germanium has been investigated also on KAD–ground carbon and on ASM silica gel modified with catechol, quinalizarin, and phenylfluorone[59], on EDE-10P anion exchanger modified with Tiron [disodium 4,5-dihydroxy benzene-1,3-disulphonate][58], and on BAU carbon modified with 8-hydroxyquinoline, tartaric and citric acids, and iron hydroxide[60–63]. In all cases modification of the sorbent led to increased sorption of germanium. However, the best results were obtained by Ziegenbalg and Scheffler on the Macroporous resin Wofatit E.[36] The use of macroporus resins as sorbent carriers is undoubtedly extremely promising for such processes. Further searches for optimum modified sorbents must be directed not only at new complexing agents but also at producing the best sorbent carriers.

Modified sorbents based on active carbons have been used to isolate uranium. A large-scale countercurrent scheme was proposed for the selective extraction of uranium from ore slurries and sulphuric-acid concentrates by walnut, coconut, and almond shell charcoals modified with di-2-ethylhexyl pyrophosphate and other organophosphorus compounds capable of chelating uranium[32,33]. These workers established also that the capacity of the modified sorbent depends on the nature of the complexing agent, its surface concentration, and the nature of the sorbent carrier.

The selective sorption of uranium from nitrate solutions containing zinc, thorium, iron, and vanadium has been accomplished[64] on BAU carbon modified with tributyl phosphate, and a method has been suggested[65] for separating uranium and iron on KAD carbon modified with 1-nitroso-2-naphthol. In the presence of trilon B at pH 4.5 to 5.5 and ratios of uranium to iron of 1 : 1–100, uranium undergoes almost complete absorption with insignificant sorption of iron. Variation in the ratio of uranium to iron within wide limits has no effect on the results of the separation.

"Alkaline A" carbon treated with phenylarsonic acid, and also arsenazo III and alkylphosphoric acids, was used for the quantitative isolation of protactinium from 1 M sulphuric acid in the presence of tin, titanium, chromium, aluminium, iron, thorium, zirconium, and uranium[35]. These sorbents were used to concentrate protactinium from uranium ores and from the products of their processing, and also to isolate protactinium from neutron-irradiated thorium.

Acetylcellulose and the vinyl chloride–acetate copolymer Corvic have been successfully used as supporting sorbents[66–68]. Microquantities of indium have been extracted on an acetylcellulose column modified with dithizone[66], and the Corvic copolymer modified with di-2-ethylhexyl hydrogen orthophosphate has been used to separate the rare-earth metals from lanthanum to lutetium. The separation was conducted from dilute perchloric acid at 60°C. Elements absorbed by the column were eluted separately in order of increasing atomic weight by perchloric acid of gradually increasing concentration[67,68].

The complexing adsorption method has been recommended also for the overall segregation of rare-earth elements from heavy metals[69,70].

7. Separation of Elements with Similar Properties

We have shown[29,43,44,71–73] that complexing adsorption chromatography offers the greatest opportunities for effecting highly selective processes in the separation of elements with closely similar properties. Niobium and tantalum, which possess similar chemical and physical

properties, were taken as the most difficult pair of elements to separate. The difficulty of separation is aggravated by the interaction of the elements, since they partly lose their individual properties when present in admixture. Aqueous solutions of their tartrate or oxalate complexes were used, with DAUKh charcoal as supporting sorbent. We find it useful to divide methods of separating niobium and tantalum into two groups, according to the complexing agents employed.

1. The modified sorbent binds mainly niobium, which is retained by the column, while tantalum passes into the filtrate with the stream of buffered solution. This enables spectroscopically pure tantalum to be isolated. Such separations have been developed by using sorbents modified with 8-hydrozyquinoline and *N*-hydroxy-*N*-phenylbenzamide. Quantitative separation of the elements can be achieved from tartrate solutions of pH 5.2–5.4 on a carbon–hydroxyquinoline sorbent at ~95°C. With a carbon–*N*-hydroxy-*N*-phenylbenzamide sorbent the best results are obtained from tartrate solutions of pH 4.5 at 95°C; a tantalum fraction free from niobium can be obtained in only ~80% yield.

2. The modified sorbent binds tantalum preferentially, while niobium passes into the filtrate with the stream of buffered solution. The niobium fraction contains the spectroscopically pure element. These results have been obtained on sorbents modified with phenylarsonic acid and tannin. Quantitative separation of the elements was obtained on both sorbents. On a carbon–phenylarsonic sorbent separation is achieved at ~95°C from oxalate media containing 0.65–1.0 *N* hydrochloric acid. On a carbon–tannin sorbent niobium and tantalum are separated from oxalate solutions of pH 2–3 at 95°C.

Complexing adsorption chromatography can be used to concentrate dilute solutions of niobium and tantalum and also for isolating these elements from a mixture. Such processes can be accomplished, for example, on a carbon–diethyldithiocarbamate sorbent, when the columns can be used many times without further regeneration.

The methods which we have proposed for isolating and separating niobium and tantalum have defined advantages over existing methods, mainly in their simplicity, the elimination of injurious and flammable organic solvents, of toxic and chemically corrosive fluorides, plus the possibility of obtaining spectroscopically pure components.

8. Separating Organic Substances and Effecting Chemical Reactions

The principle underlying complexing adsorption chromatography can obviously be used not only for the separation of inorganic substances but also in organic chemistry to accomplish certain chemical reactions and to separate organic compounds.

Forster and Rogers[74] separated amines on columns comprising silica gel or aluminium oxide treated with inorganic salts. Modification was shown to improve the selectivity and increase the capacity of the sorbents. As in the separation of inorganic products, sorption is described by the Langmuir equation. Balint[75] separated the aromatic components of solar distillates on an aluminosilicate treated with picric acid.

9. Use of Modified Sorbents under Static Conditions

We have been discussing the chief ways in which modified sorbents can be used chromatographically, i.e. on columns under dynamic conditions. Sometimes, however, it is desirable to apply them under static conditions, e.g. at the enrichment stage in the selective sorption of elements from slurries and lyes and in some other cases.

Lodeishchikov and Panchenko showed[76] that the isolation of gold and silver from the difficultly filterable slurries formed in the processing of an argillaceous ore can be suitably and economically accomplished by stirring the slurry vigorously with a suspension of carbon in the presence of thiourea. With gold and silver contents in the slurry of 7.8 and 3.2 g t^{-1} respectively the total content of noble metals after isolation on carbon was given as 240 to 250 kg t^{-1}.

Kuzin et al.[77] investigated the sorption of uranium, cerium, thorium, iron, and magnesium on SKT active carbon from acetic-acid solutions, and found that under these conditions uranium is sorbed selectively and can be separated from the other components of the mixture. Desorption of the uranium with 1 *N* hydrochloric acid enables a high degree of concentration to be achieved.

Similar results were obtained by Kogan and Evdokimov[78,79] for the sorption of germanium from oxalate solution on BAU active carbon. They found that the molecular proportions of germanium and oxalic acid sorbed approximated to the ratio in the complex $H_2[Ge(C_2O_4)_3]$.

It must be borne in mind, however, that in the static variant we lose the advantages of the chromatographic method, i.e. the possibility of separating sorbable substances on a column and maximum utilisation of the capacity of the sorbent.

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Study of the mechanism of the complexing adsorption of metals enables paths for its further development to be mapped out, and possible limits to and the advisability of its application for practical purposes to be assessed.

We have investigated the mechanism and the kinetics of the absorption of metal ions on modified sorbents in which the carrier was DAUKh charcoal[28,29]. Several regularities which were then established—the molecular character of the sorption of complexing agents and their reaction products with metal ions, the inner-diffusion kinetic mechanism, and the occurrence of a second-order chemical reaction—can be regarded as general features of the method, as is shown by the kinetics of the process. At the same time there are also specific features of the mechanism resulting from the properties of active carbon as a carrier—the simultaneous occurrence of two sorption mechanisms (ion exchange and molecular) and the effect of the character of the pores on the sorption processes, as evident in the dependence of the degree of utilisation of the complexing agent on coverage of the sorbent carrier by the agent, on the retention time of the modified sorbent, and on the temperature.

Investigations of the mechanism and the kinetics of absorption on other sorbents, which can subsequently be used as supports for complexing agents, should be of considerable interest for the development of complexing adsorption chromatography. A promising field is the application of the recently synthesised macroporous and isoporous resins, which are capable of the molecular sorption of organic compounds. Perhaps these carriers will yield modified sorbents with better kinetic characteristics and greater utilisation of the modifier than in the case of sorbents based on active carbon. However, the application of active carbon in the complexing adsorption

method is not yet exhausted, and continued examination of the properties of this extremely interesting sorbent is required, so that all its inherent possibilities can be more fully exploited.

Active carbon is most convenient in industrial and semi-industrial preparations because of its cheapness, mechanical durability, and chemical resistance. The radiation resistance of carbon enables it to be used to separate radioactive preparations at various stages in the processing of ores. For example, Davydov et al.[35] used active carbon saturated with phenylarsonic and alkylphosphoric acids to concentrate protactinium from uranium ores and their products, and also for isolating protactinium from neutron-irradiated thorium. The yield of protactinium exceeded 90%. Modified carbon can be used[44] to purify radioactive isotopes.

The complexing adsorption method should play a quite important part in the isolation of rare and trace elements and in the separation of elements having closely similar properties[29,43,44,71-73].

Study of a series of complexing adsorption systems has shown that an unlimited range of highly selective sorbents having specified properties can be prepared by the simplest methods, by exploiting for this purpose the rich opportunities provided by the different kinds of complexing agents available to the chemist[80]. Some ways of preparing such modified sorbents have been discussed above.

Even at this stage in the development of complexing adsorption chromatography the analytical chemist is already able to select a modified sorbent for the overwhelming majority of separation processes, by skilfully exploiting the properties of separable and complexing substances.

The practical application of complexing adsorption chromatography has shown that it is most suitably employed for purifying substances which are not sorbed in the column from impurities present in minute concentrations and retained by the modified sorbent. With other concentration relations of the elements to be separated the advisability of using this method would be determined by economic considerations taking into account the possibility of regenerating the modified sorbent.

The broad development of the complexing adsorption method and its introduction into industry require the production of special sorbent carriers possessing mechanical, chemical, and radiation stability, a high capacity for various kinds of organic compounds, good kinetic and hydrodynamic characteristics, and a structure which would ensure full utilisation of the modifier independently of its amount on the carrier.

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Oxygen Fluorides and Dioxygenyl Compounds

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The review considers the methods of preparation, structures, and properties of oxygen fluorides and dioxygenyl compounds which are genetically related to them.
The bibliography includes 124 references.

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I. INTRODUCTION

The oxygen compounds of the halogens constitute one of the groups of compounds of the most electronegative elements. Substances of this kind are oxidants with a high energy store, which are capable of releasing their chemical energy under certain conditions either instantaneously or at a controlled rate. Compounds of fluorine and oxygen are of special interest in this sense, since they comprise light electronegative atoms.

The chemical bond between oxygen and the halogens is covalent. The names adopted for the binary compounds of oxygen and halogens—"oxygen fluorides" and "chlorine, bromine, and iodine oxides"—reflect the electronegativity of the elements and are consistent with the rules of the International Union of Pure and Applied Chemistry (IUPAC).

This review deals with oxygen fluorides, the methods for their preparation, and their physical properties, structures, and reactions. The existing reviews[1-3] no longer embrace the entire accumulated experimental data. The authors of the present review do not claim an exhaustive presentation of the subject, their aim being to examine mainly studies published after the extensive review by Streng[1].

One of the most important properties of oxygen fluorides is their capacity to react with fluorine-containing Lewis acids forming dioxygenyl salts. Dioxygenyl hexafluoroplatinate, the first compound of the O_2^+ cation (obtained by Hartlett[4]), preceded and simulated the synthesis of valence compounds of xenon[5]. These studies had a significant influence on the development of modern refined inorganic syntheses. Dioxygenyl compounds are considered in a separate section of the present review.

II. OXYGEN FLUORIDES

1. Oxygen Difluoride

Oxygen difluoride has been known since 1927.[6] A widely employed method for the separation of OF_2 is based on the reaction of gaseous fluorine with a dilute aqueous solution of alkali[1,7]:

$$2F_2 + 2NaOH\ (KOH) \rightarrow OF_2 + 2NaF\ (KF) + H_2O\ .$$

Oxygen difluoride is also obtained by the electrolysis of hydrogen fluoride containing added water and an alkali metal fluoride[1,8]. Recently the reaction of fluorine with water in the presence of an alkali metal (Na, K, and Cs) fluoride was proposed as a method for the preparation of OF_2.[9] The synthesis is carried out in a glass apparatus where the HF and SiF_4 formed combine with the metal fluoride and do not contaminate the desired product, the yield of which reaches 80%.

Oxygen difluoride is thermally stable up to 200–250°C. It melts at −224°C, the yellow liquid boiling at −145°C; the vapour pressure of OF_2 is 1 mmHg at −196°C and 11 mmHg at −183°C.[1] Probably the most reliable value of the standard enthalpy of formation, $\Delta H^\circ_{f298}[OF_{2(gas)}] = 5.86 \pm 0.38$ kcal mole^{-1}, has been obtained[10] by measuring the heat of combustion of hydrogen in OF_2. The average thermochemical energy of the O–F bond in the OF_2 molecule is 45.7 kcal mole^{-1}.[10] The dissociation energy of the first O–F bond is less than the dissociation energy of the second bond; for example, $D(F-OF) \simeq 42.7$ and $D(OF) \simeq 48.3$ kcal mole^{-1} have been quoted[11].

The geometrical parameters of the OF_2 molecule have been determined by microwave spectroscopy[12]: $r(O-F) = 1.390$ Å and $\angle FOF = 104°16'$, differing somewhat from $r(O-F) = 1.412$ Å and $\angle FOF = 103°10'$ obtained by Pierce et al.[13] The infrared spectrum of gaseous OF_2 contains three intense bands corresponding to three normal vibrations: 928 (symmetrical stretching), 461 (deformation), and 831 cm^{-1} (antisymmetric stretching) and a number of weak absorptions—overtones and compound frequencies: 1281, 1648, 1728, 1740, 1840, 2188, 2455, 2643 cm^{-1}.

Oxygen difluoride is an effective fluorinating agent, somewhat inferior in reactivity to elemental fluorine[15]. In systems subjected to the action of an electric discharge or radiation, oxygen difluoride both fluorinates and oxidises. The reaction of OF_2 with unsaturated nitrogen fluorides in an electric discharge results in the formation of nitrogen trifluoride, oxide fluorides, and oxide[16]. By exposing oxygen difluoride and NF_3 to an electric discharge, it is possible to obtain trifluoroamine oxide[17,18]. A photochemical reaction of OF_2 with chlorine trifluoride has been used to synthesise chlorine oxide trifluoride $ClOF_3$.[19] When ionising radiation acts[20] on a mixture of NF_3 and OF_2 at −196°C, O_2F_2 and N_2O_4 are formed. XeF_2 and KrF_2 have been obtained by the photochemical fluorination of xenon[21] and krypton[22]. By heating a mixture of xenon and oxygen difluoride to 400°C or passing a mixture of the reactions through a discharge, XeF_4 and xenon oxide fluorides have been synthesised[1]. Oxygen difluoride does not react with liquid chlorine, or with gaseous chlorine at a moderate temperature, but in an electric discharge at low temperatures a reaction leading to the formation of ClF, ClO_2, and ClO_2F takes place[16].

The primary stage in the thermal reactions of oxygen difluoride with nitrogen dioxide[23] and tetrafluorohydrazine[24] is the abstraction of a fluorine atom from the OF_2 molecule:

$$(N_2O_4 \rightleftarrows 2NO_2)\ NO_2 + FOF = FNO_2 + OF,$$
$$(N_2F_4 \rightleftarrows 2NF_2)\ NF_2 + FOF = NF_3 + OF\ . \qquad (*)$$

The activation energy for reaction (*) is 22.5 kcal mole^{-1}. We may note for comparison that the activation energy for the reaction

$$NF_2 + F_2 = NF_3 + F$$

is only 9.7 kcal mole^{-1}.[25] The reaction of oxygen difluoride with tetrafluorohydrazine,

$$2N_2F_4 + OF_2 = FNO + 3NF_3\ ,$$

gives rise to nitrosyl fluoride, which does not react with oxygen difluoride below 170°C.[24]

Certain reactions involving oxygen difluoride may be regarded as addition to the second reactant of a fluorine atom and an OF radical—fragments derived from OF_2. When radiation at a wavelength of 3650 Å was allowed to act on a mixture of OF_2 and SO_3 at room temperature, fluoroperoxy-sulphuryl fluoride FSO_2OOF was obtained[26,27]. If the radiation includes quanta the energy of which is sufficient for the excitation of sulphur trioxide, then FSO_2OOF is formed in trace amounts and the main reaction products are pyrosulphuryl fluoride and sulphuryl fluoride[28]. The fact that the OF group in fluoroperoxysulphuryl fluoride originates from oxygen difluoride was demonstrated[29] in a study of the reaction of OF_2 and SO_3 by a tracer atom method, the products being analysed by ^{17}O NMR. The photochemical reaction of oxygen difluoride with peroxydisulphuryl difluoride[28] yields FSO_2OOF and FSO_3F. The reaction probably takes place as follows:

$$(1)\ F_2S_2O_6 \rightleftarrows FSO_3 + FSO_3,\ (2)\ OF_2 \rightarrow F + OF,$$
$$(3)\ FSO_3 + F = FSO_3F, \qquad (4)\ FSO_3 + OF = FSO_2OOF\ .$$

The photochemical reaction of OF_2 with sulphur dioxide gave pyrosulphuryl fluoride and sulphuryl fluoride[28], whereas on heating OF_2 and SO_2 to 300–500°C sulphuryl and thionyl fluorides are formed[30].

The reaction of oxygen difluoride with primary amines[31] leads to the formation of nitroso-compounds or oximes, for example nitrosocyclopropane has been obtained by the oxidation of cyclopropylamine at −42°C. It is believed that the interaction of OF_2 with amines can be described in terms of the following mechanism[31]:

$$RNH_2 + OF_2 \rightarrow [\overset{(+)}{R}NH_2{-}OF]\overset{(-)}{F} \longrightarrow RN{=}O + 2HF$$
$$\underset{\text{or}}{\downarrow} [RNH{-}OF] + HF \longrightarrow \uparrow\ .$$

One of the intermediate stages in the low-temperature (−78° or −40°C) oxidation of olefins and alkynes by oxygen difluoride probably involves the addition of F–OF to the double or triple bond[32]. Perfluoroethylene, perfluoropropene, perfluorobut-2-ene, and perfluorocyclobutene are less reactive with respect to oxygen difluoride: the reactions of these compounds with OF_2 require thermal or photochemical activation[33]. It is believed that in this case the OF_2 molecule adds to the double bond, but the resulting hypofluorites undergo further reactions, as in the reaction between OF_2 and unsaturated hydrocarbons. When OF_2 reacts with tetramethylallene, the hypofluorite (I) may be formed as an intermediate, which is converted further into compounds (II) and (III):[34]

$$Me_2C{=}C{=}CMe_2 \xrightarrow[-78°]{OF_2} \left[Me_2C{=}\underset{\underset{FO\ \ F}{|\ \ \ |}}{C}{-}CMe_2\right] \rightarrow Me_2\underset{\underset{F\ O\ F}{|\ \ \|\ \ |}}{C}{-}CMe_2 +$$
(I) (II)
$$+ Me_2\underset{\underset{F\ \ O}{|\ \ \|}}{C}{-}C(Me){=}CH_2 + HF\ ,$$
(III) (Me=CH$_3$)

The thermal (at 50–90°C) or photochemical (λ = 3660 Å; 0°C) reaction of oxygen difluoride with carbonyl sulphide[35], $OF_2 + S = CO \rightarrow F_2SO + CO$, may be regarded as yet another example of the addition of OF_2.

The reaction of oxygen difluoride with carbonyl fluoride in the presence of a catalyst (CsF for RbF) at 25°C gave bis(trifluoromethyl) trioxide[36]: $OF_2 + 2F_2CO = CF_3OOOCF_3$. CF_3OOOCF_3 is formed in low yields when sodium trifluoroacetate is fluorinated[37]. CF_3OOOCF_3 is quite stable at room temperature, decomposing slowly at

70°C with formation of CF_3OOCF_3 and oxygen. The catalytic synthesis of CF_3OOOCF_3 proceeds via several stages[36,38]:

$$(1)\ COF_2 + MF \rightarrow M^+OCF_3^-, \qquad (2)\ OF_2 + CF_3O^- \rightarrow CF_3OOF + F^-,$$
$$(3)\ CF_3OOF + CF_3O^- \rightarrow CF_3OOOCF_3 + F^-, (4)\ CF_3OOF + COF_2 \rightarrow CF_3OOOCF_3.$$

Yet another method for the preparation of bis(trifluoromethyl) trioxide was described recently[39]: it involves the reaction of carbonyl fluoride with di(fluoroxy)difluoromethane in the presence of CsF. Simultaneously with the work of Anderson and Fox[39], a method was described for the preparation of CF_3OOOCF_3 by the reaction of $F_2C(OF)_2$ with caesium trifluoromethoxide in the presence of CsF.[40] In addition to bis(trifluoromethyl) trioxide, CF_3OF, $CF_3OOC(O)F$, and $CF_3OOOCF_2OOCF_3$ are formed by this reaction. The last compound is much less stable than CF_3OOOCF_3 or $CF_3OOOC_2F_5$ and decomposes explosively at 40°C.

The hypothesis postulating oxygen difluoride as a source of OF radicals in reactions involving it appears fairly reasonable. The possibility of the stabilisation of the OF group as a cation must be viewed with restrained optimism: even one of the most probable compounds in which OF^+ might exist, namely $[FO]^+[SbF_6]^-$, could not be obtained by the reaction of OF_2 and SbF_5,[16,41] although the OF_2 molecule, which has the same electronic structure as the OF^+ cation, exists and is quite stable.

In connection with the search for methods of synthesising OF radicals, the behaviour of oxygen difluoride was studied in recent years under conditions leading to its dissociation. The photochemical decomposition of OF_2 in the temperature range 15–45°C has the following mechanism[42]:

$$OF_2 \xrightarrow{h\nu,3650\ Å} F + OF,$$
$$F + F + M = F_2 + M,$$
$$OF = {}^1/_2F_2 + {}^1/_2O_2 .$$

The slow reaction $F + OF_2 = F_2 + OF$, the activation energy of which exceeds 15 kcal mole^{-1},[42] is also possible.

The thermal decomposition of OF_2 into fluorine and oxygen has been investigated[43] in a nickel flow reactor at temperatures in the range 500–700°C. The OF radicals were not detected mass-spectrometrically in the samples removed from the reactor: the ratio of the peak intensities for $m/e = 35$ (OF) and 54 (OF_2) did not differ from the ratio usually observed in the mass spectrum of OF_2. Nor were OF radicals detected in a study of the pyrolysis of OF_2 on heated metallic filaments[44]. The attempt at a mass-spectrometric detection of OF radicals in a stream of oxygen difluoride passed through a microwave discharge also proved unsuccessful[44]. OF radicals were not found to accumulate in an OF_2 specimen subjected to ionising radiation at −196°C.[20]

The mechanism of the decomposition of OF_2 in a shock wave (590–1030°C) and in a static reactor (290–360°C) has been discussed[45,46]. The decomposition of OF_2, which begins after a short induction period, proceeds for a time as a first-order reaction[46], but the overall kinetics of the thermal composition of OF_2 are not consistent with a unimolecular reaction[43,46]. The addition of oxygen does not influence the rate of the thermal decomposition of OF_2 and the addition of fluorine inhibits it. It is suggested[11] that the inhibiting effect of fluorine can be accounted for by the reaction $F_2 + OF = OF_2 + F$. Analysis of the literature data[43,45–47] and the results obtained in a study of the decomposition of OF_2 in a shock wave tube (500–1120°C) enabled Lin and Bauer[11] to suggest a mechanism for the thermal decomposition of OF_2 similar to that for the photochemical decomposition:

$$OF_2 + M \overset{a}{\rightleftarrows} F + OF + M,$$
$$2\,OF \xrightarrow{b} 2F + O_2,$$
$$2F + M \rightleftarrows F_2 + M .$$

Reaction (a) determines the rate of decomposition, its activation energy being 30–40 kcal mole^{-1} according to a number of data[11,43,45–47]. In the temperature range 500–960°C, $k_a = 10^{16.7}\exp(-45\,500/RT)$ cm^3 mole^{-1} s^{-1}.[48] The following mechanism has been postulated for reaction (b):

$$FO + OF \rightarrow (F{-}O{-}O)^* + F + 30\ \text{kcal (fast)},$$
$$(FO_2)^* \rightarrow F + O_2\ \text{(very fast)}.$$

The existence of OF radicals could be demonstrated only with the aid of the matrix isolation technique combined with infrared spectroscopy[49]. The radicals were obtained by the photolysis of OF_2–N_2 or OF_2–Ar mixtures deposited on caesium bromide with the ratio of the number of moles of the matrix to the number of moles of the reactant $M/R = 40$. The absorption band at 1028 cm^{-1} in an argon matrix and a doublet at 1025 and 1030 cm^{-1} in a nitrogen matrix arose after the photolysis of the mixtures deposited at 4°K and disappeared on heating the matrix to 40–45°K. The frequency shift observed in the spectra on photolysis of $^{18}OF_2$ agrees with the calculation on the assumption that the absorption is due to the OF radical. The vibration frequency of the OF radical is 1028 cm^{-1}—the maximum frequency of the OF stretching vibrations in the compounds, including OF_2. Special experiments with the addition of nitrous oxide to the mixture of gases deposited for photolysis revealed the cause of the appearance of a doublet in the nitrogen matrix. The 1025 cm^{-1} band is due to OF radicals in matrix cages containing N_2O and the 1030 cm^{-1} band is due to OF radicals in cages without N_2O. Nitrous oxide is formed as an impurity in the isolating matrix by the reaction of atomic oxygen with N_2 molecules. The low efficiency of the emission at a wavelength of 3650 Å in relation to the generation of OF radicals, compared with gas-phase reactions[26,42], indicates an appreciable role of the cage effect in the matrix photolysis of OF_2.

The yield of OF radicals increases appreciably in the photolysis of OF_2 in a nitrogen matrix in the presence of nitrous oxide or carbon dioxide[50]. One of the pathways for the destruction of radicals is the recombination reaction $F + OF = OF_2$. In the presence of nitrous oxide fluorine atoms are consumed in the reaction

$$F + N_2O \rightarrow OF + N_2 \qquad (**)$$

which constitutes an additional source of OF radicals. According to reaction (**), the lower limit of the bond energy in the OF radical may be estimated as about 40 kcal. An increase of the yield of OF radicals was achieved also in experiments with added CO_2, but the mechanisms of the action of the CO_2 and N_2O additives are different. Fluorine atoms do not react with carbon dioxide under the conditions of matrix photolysis:

$$F + CO_2 \not\rightarrow OF + CO .$$

Probably the following reactions take place in the photolysis of an OF_2–CO_2 mixture:

$$O + CO_2 \rightarrow CO_3,$$
$$F + CO_3 \rightarrow OF + CO_2 .$$

It is also possible that the presence of CO_2 in the matrix and the reaction

$$O + CO_2 \overset{h\nu}{\rightleftarrows} CO_3$$

extend the migration region of O atoms and increase thereby the probability of the reaction $O + F \rightarrow OF$.

The strength of the bonds in the OF radical is sufficiently high for the radicals to exist as stable entities, for example at room temperature. The numerous unsuccessful attempts to detect OF radicals in the gas phase are evidence of their extremely high reactivity. The stabilisation of OF is possible only in an inert matrix over a very narrow temperature range.

2. The Reaction of Fluorine with Oxygen

The term "polyoxygen difluorides" embraces oxygen fluorides the molecules of which contain more than one oxygen atom. Polyoxygen difluorides are very unstable compounds, which decompose considerably below room temperature. They cannot be obtained simply by heating a mixture of fluorine and oxygen. Nevertheless at an elevated temperature fluorine interacts with oxygen and if provision is made for the stabilisation of the reaction products, the fluorine–oxygen compound formed may be isolated. When fluorine and oxygen are passed through a quartz reactor heated to 240–500°C with subsequent quenching of the gases by contact with a surface cooled to −196°C, it is possible to obtain O_2F radicals in an amount sufficient to record their ESR spectrum [51]. In the synthesis of dioxygenyl compounds by heating fluorine, oxygen, and arsenic or antimony pentafluorides to 130–200°C, [41] O_2F radicals are probably formed initially:

$$F_2 \rightleftarrows 2F,\ O_2 + F \rightarrow O_2F,$$

and then react further with the Lewis acid:

$$O_2F + AsF_5\ (SbF_5) = O_2AsF_6\ (O_2SbF_6).$$

The stabilisation of unstable species with the aid of a powerful Lewis acid is a procedure widely employed in inorganic synthesis.

Polyoxygen difluorides are synthesised from the elements in a glow discharge where the reaction of fluorine with oxygen under optimum conditions goes almost to completion. The reaction is carried out in a quartz or pyrex discharge tube, the walls of which are maintained at a low temperature. In experiments at a low current, the electrodes consist of copper or nickel plates inserted into the tube with the aid of Teflon stoppers or in some other way. If the experiments are performed at a discharge current exceeding about 50 mA, the electrode shells are cooled with tap water. A stream of a fluorine–oxygen mixture is passed through the discharge at a reduced pressure. The residual pressure in the apparatus is unimportant when polyoxygen difluorides are obtained in a glow discharge. The pressure is maintained in the range from a few tenths to several mmHg. The Table summarises certain data for the reaction of O_2 and F_2 in a glow discharge. The synthesis of O_2F_2, O_3F_2, and O_4F_2 in an electric discharge from oxygen difluoride and fluorine [52] is analogous to the syntheses of the above compounds from the elements and is of no preparative interest, since oxygen difluoride is less readily available as a starting material than oxygen.

Apart from the flow discharge, the silent and arc discharges are sometimes employed for the synthesis of organic compounds. The reaction of fluorine with oxygen in discharges of this type has not been investigated in sufficient detail. The authors of a study [57] published in 1909 did not obtain oxygen fluoride by passing fluorine and oxygen through an arc discharge and a tap cooled with liquid air. In subsequent years the synthesis of oxygen fluorides in an electric arc was apparently not investigated. The synthesis of O_2F_2 and O_4F_2 in a silent discharge cannot compete as regards the yield of products per unit time and the energy yield with the synthesis of these compounds in a glow discharge and is of interest only within the framework of the study of the mechanism of the reaction of fluorine and oxygen in electric discharges.

Preparation of polyoxygen difluorides.

Reaction equation	Refs	Typical conditions of synthesis			
		compn. of initial mixt. (F_2:O_2 by volume)	flow rate, litre h^{-1}*	Current, mA	Temp. of cooling bath, °C
$O_2 + F_2 = O_2F_2$	53	1:1	~1—~10	~10—~50	−196 or −183
$3O_2 + 2F_2 = 2O_3F_2$	54	2:3	2—2.5	25—30	−196 or −183
$2O_2 + F_2 = O_4F_2$	55	1:2	0.12	4—5	from −213 to −196
$5O_2 + 2F_2 = 2O_5F_2$	56	2:5	0.006—0.008	power ~ 5 W	−213 (−196)
$3O_2 + F_2 = O_6F_2$	56	1:3	0.015—0.022	Power 2-6 W	−213

*Volumes under normal conditions.

Dioxygen difluoride with an admixture of other polyoxygen difluorides was obtained by the action of ionising radiation on a mixture of fluorine and oxygen at −196°C. [58] The apparatus used in this method of synthesis is more complex than the apparatus necessary to synthesise dioxygen difluoride in a discharge. The radiolysis of oxygen difluoride at −196°C leads to the decomposition of OF_2 into the elements with formation of a certain amount of dioxygen difluoride [20].

The available literature data suggest that a gas-phase photochemical reaction can occur between fluorine and oxygen. By keeping a mixture of fluorine, oxygen, and AsF_5 or SnF_5 in the light, the dioxygenyl salts O_2AsF_6 and O_2SbF_6 were obtained [59]. Probably the O_2F radical formed initially reacts with the Lewis acid ($O_2F + EF_5 = O_2EF_6$) as in the thermal reaction [41]. When a mixture of fluorine and oxygen was irradiated by light from a mercury lamp, the formation of dioxygen difluoride was noted [60]. Bearing in mind that appreciable decomposition of O_2F_2 begins at a temperature as low as −100°C, [61] it is very remarkable that the experiments of Levy and Copeland were carried out at −42°C.

As a result of the irradiation of a mixture of fluorine and ozone with ultraviolet light in a reaction vessel thermostatted at −153°C, [62] O_2F_2 and OF_2 were formed. It is suggested that the reaction proceeds as follows:

$$F_2 \xrightarrow{h\nu,\,3650\,Å} 2F,\ F + O_3 \rightarrow O_2 + OF,$$

$$OF + OF = O_2F_2,\ OF + F = OF_2,\ OF + F_2 = OF_2 + F.$$

In analogous experiments at −78°C only oxygen difluoride was obtained [62]. If the photochemical reaction of fluorine with oxygen is carried out at a still higher temperature (0°C and 20°C), the decomposition of ozone without the formation of oxygen fluorides is observed [63]:

$$F_2 + O_3 \xrightarrow{h\nu,\,3650\,Å} F_2 + {}^3/_2O_2.$$

Among all the reactions enumerated and leading to the formation of dioxygen difluoride and other polyoxygen

difluorides, only the reaction of fluorine with oxygen in a glow discharge can be regarded as a simple and readily available method of synthesis of polyoxygen difluorides.

The most probable mechanism of the synthesis of polyoxygen difluorides from the elements includes as the primary step the reaction of atomic fluorine with molecular oxygen:

$$F + O_2 = O_2F$$

and further stages involving O_2F radicals, for example:

$$O_2F + F = O_2F_2,$$
$$O_2F + O_2F = O_4F_2,$$
$$O_2F + O_2 \rightarrow O_4F \xrightarrow{+O_2F} O_6F_2 .$$

In this mechanism the dissociation of O_2 molecules is not regarded as an essential stage of the synthesis. Possibly, in general any activation of oxygen is superfluous. Irradiation of F_2–O_2 mixtures under matrix conditions at 4° or 20°K by ultraviolet light, which dissociates only fluorine molecules, leads to the formation of O_2F radicals[64,65]. Atomic oxygen is probably formed when F_2–O_2 mixtures are passed through a glow discharge, but in this case too there is no need to include in the mechanism for the synthesis of polyoxygen difluorides reactions involving atomic oxygen. An equimolar fluorine–oxygen mixture is almost completely converted into O_2F_2 with a low energy expenditure per unit volume of the reacting gases with a negligibly low degree of dissociation of oxygen[66]. With increase of energy expenditure, the dissociation of O_2 molecules becomes more pronounced and the synthesis of O_2F_2 is accompanied by the formation of ozone as a side reaction.

The preparation of unstable polyoxygen difluorides has been fairly thoroughly investigated, but a method for the synthesis of the thermally stable oxygen difluoride from the elements is unknown. The formation of trace amounts of OF_2 in the synthesis of O_2F_2 has been noted[44] but the possibility of obtaining OF_2 in an appreciable yield in a glow discharge is doubtful. The formation of O_2F_2 or another polyoxygen difluoride, which does not require the dissociation of O_2 molecules, has a clear advantage over the synthesis of OF_2. Under the conditions where the degree of dissociation of O_2 becomes appreciable, the formation of OF_2 may be hindered by the consumption of O atoms in the synthesis and decomposition of oxone: $O + O_2 = O_3$ and $O_3 + O = 2O_2$. One must also assume the possibility of the recombination of OF radicals with formation of O_2F_2:

$$OF + OF = O_2F_2 (S),$$

where (S) is a cold wall. Finally it is extremely likely that the absence of OF_2 from the product of the reaction of fluorine with oxygen in a glow discharge is simply due to the high vapour pressure of OF_2, which is about 1 mmHg at −196°C. It is difficult to freeze a substance with such a vapour pressure on the cold wall of the discharge tube and thereby prevent its decomposition in the hot reaction zone.

3. Dioxygen Difluoride

In order to prepare dioxygen difluoride, an equimolar mixture of fluorine and oxygen or one containing a slight excess of fluorine is passed through a glow discharge[53,67,68]. Dilution of the initial equimolar mixture with argon hardly alters the degree of its conversion into dioxygen difluoride[66]. When fluorine, oxygen, and nitrogen are passed through a glow discharge in a low-temperature reactor, dioxygen difluoride is also formed but in this case a certain amount of oxygen also enters into the reaction as a result of which trifluoroamine oxide is formed[69].

The dioxygen difluoride obtained in the glow discharge is sometimes contaminated by one or several substances, for example SiF_4 and O_4F_2. The decomposition of the less stable oxygen fluorides present in the freshly prepared O_2F_2 specimen can probably account for the increase of pressure in a closed system observed when O_2F_2 is heated to a temperature close to −160°C. Usually the impurity content is small and does not affect appreciably the results of the chemical analysis of O_2F_2 and does not prevent its further employment. Brief heating above −78°C causes partial decomposition of O_2F_2 and therefore O_2F_2 can be distilled from one compartment of a closed system to another, without removing by the vacuum pump a "cushion" of fluorine and oxygen, only with the aid of liquid helium.

Dioxygen difluoride melts at −163.5°C [53] (−154°C according to later data[70]) and decomposes below the boiling point; the normal boiling point found by extrapolating the the temperature variation of the vapour pressure is −57°C.[61] Solid O_2F_2 is orange-yellow in colour (yellow according to some observations[58,70]), turning into an oily bright-red liquid on fusion. With increase of temperature, the molar extinction coefficient of O_2F_2 rises[71]. The density of O_2F_2 decreases from 1.912 g cm^{-3} at −165°C to about 1.44 g cm^{-3} at −57°C.[61] The vapour pressure of O_2F_2 in the temperature range between −132° and −100°C is described by the equation[61] $\lg p$ (mmHg) = 7.515 − $1000/T$, the decomposition of O_2F_2 beginning above −100°C. The vapour pressure of O_2F_2 is (in mmHg) 0.01 at −168°C,[1] 0.05 at −163°C,[72] 1 at −143°C,[72] 3 at −132°C,[61] and 257 at −79.5°C.[61] $\Delta H^{\circ}_{f_{298}}[O_2F_2(gas)]$ found in a study of the decomposition of dioxygen difluoride is 4.73 kcal mole^{-1}.[73]

It has been established by microwave spectroscopy[74] that the O_2F_2 molecule consists of an F–O–O–F atomic chain bent in space and characterised by the following parameters: r(O–O) = 1.217 Å, r(O–F) = 1.575 Å, ∠ OOF = 109°30′, a dihedral angle of 87°30′, and a dipole moment of 1.44 D. Quantum-mechanical calculation shows[75] that the configuration of the O_2F_2 molecule with a dihedral angle of 85°C is separated from the *cis*- and *trans*-configurations by energy barriers of 16.62 and 20.83 kcal mole^{-1} respectively. The spectrum of $^{16}O_2F_2$ recorded at −196°C contains absorption bands at 1306 cm^{-1} (O–O stretching vibration), 621 cm^{-1} (O–F symmetrical stretching vibration), 615 cm^{-1} (O–F antisymmetric stretching vibration), 457 cm^{-1} (O–O–F antisymmetric deformation vibration), 369 cm^{-1} (O–O–F symmetrical deformation vibration), and 205 cm^{-1} (torsional vibration)[70,76]†.

The dioxygen difluoride molecule is diamagnetic. Pure O_2F_2 molecules do not give rise to an ESR signal[58]. The paramagnetic centres in dioxygen difluoride are the O_2F radicals[77,78] the presence of which can be accounted for by the partial decomposition of the compound.

An unusually low ^{19}F chemical shift (−865 p.p.m.) has been found[79] in O_2F_2 (10% solution of O_2F_2 in CF_3Cl), which is evidence of very weak screening of the fluorine nuclei. Subsequent studies[80–82] confirmed this report[79]. δ = −865 p.p.m. was found for liquid O_2F_2 at −128°C using $CFCl_3$ as an external standard[81]. Extrapolation to

† After this paper had been sent to the Editors, D. J. Gardiner, N. J. Lawrence, and J. J. Turner published the results of a study of the vibrational spectra of O_2F_2 [J. Chem. Soc., A, 400 (1971)].

infinite dilution of O_2F_2 in CF_3Cl at −83°C gave δ = −825 p.p.m.[82] The ^{17}O shift in the $^{17}O_2F_2$ molecule is[80,83] −647 p.p.m. relative to $H_2{}^{17}O$.

The O–O distance in the O_2F_2 molecule is close to the interatomic distance in the oxygen molecule (1.207 Å), r(O–F) in O_2F_2 considerably exceeds r(O–F) in the OF_2 molecule (1.39–1.41 Å). With these interatomic distances, there should be a strong O–O bond and a weak O–F bond in O_2F_2. The following dissociation energies have been found mass spectrometrically[72]: D(FO–OF) = 103.5 ± 5 kcal mole^{-1} and $D(F-O_2F) \simeq D(O_2-F) \simeq 18$ kcal mole^{-1}. The fluorine atoms weakly bound to oxygen are readily split off as a result of which O_2F_2 is extremely reactive even at a low temperature.

The kinetics of the thermal decomposition of dioxygen difluoride have been investigated as early as the 1930's.[67,84,85] In the temperature range between −60° and −25°C the decomposition reaction is homogeneous and unimolecular with an activation energy of about 17 kcal mole^{-1}. As was to be expected, the activation energy for the decomposition is almost identical with the O–F bond dissociation energy. Addition of fluorine activates the decomposition of O_2F_2.[85] The most probable decomposition mechanism[11] involves O_2F radicals:

$$O_2F_2 + M \rightarrow F + O_2F + M,$$
$$O_2F + M \rightarrow F + O_2 + M,$$
$$F + O_2F_2 \rightarrow F_2 + O_2F,$$
$$F + F + M \rightarrow F_2 + M\ .$$

The decomposition mechanism[86] the initial stage of which is the formation of OF radicals,

$$O_2F_2 \rightarrow OF + OF\ ,$$

is unlikely, since it requires a considerable activation energy[11]. The method of chemical analysis of dioxygen difluoride is based on the determination of the amount of fluorine and oxygen obtained after the decomposition of O_2F_2.

The O_2F radical, detected by infrared spectroscopy in the photolysis of OF_2–O_2 or F_2–O_2 mixtures under matrix isolation conditions[64,65,87], plays an important role in the chemistry of low-temperature oxygen fluorides. It has also been noted[64] that O_2F radicals are generated when oxygen difluoride is exposed to an ultrahigh frequency glow discharge. When the matrix isolating the radicals (oxygen, nitrogen, or argon) becomes softened, recombination takes place[64]:

$$O_2F + F = O_3F_2,$$
$$O_2F + O_3F = O_4F_2\ .$$

The dioxygen monofluoride radical consists of the atomic chain O–O–F. Quantum-mechanical calculation[88] shows that the asymmetric OOF structure is energetically more favourable to the extent of almost 100 kcal mole^{-1} compared with the symmetrical structure OFO. The vibration frequencies in the infrared spectrum of $^{16}O_2F$ are[87] 1495 (ν_1), 585 (ν_2), and 376 cm^{-1} (ν_3). The force constant k_{O-O} for O_2F is close to the value in the oxygen molecule and lies in the range 8–12 mdyn Å^{-1} characteristic of double bonds:

	k_{O-O}, mdyn Å^{-1}		
O_2F	10.45[64]	10.47[65]	10.50[87]
O_2	11.43[89]		

The dissociation energy of the O–O bond in O_2F is 110 kcal according to mass-spectrometric data[72,90], i.e. the addition of the F atom to the O_2 molecule does not result in an appreciable loss of strength by the O–O bond. The average lifetime of dioxygen monofluoride depends on the surrounding medium and at temperatures between −180° and −160°C amounts to minutes[91]. Generally speaking the dioxygen monofluoride radical resembles stable molecular radicals more than unstable radicals such as OF. If the interpretation[92] of the results obtained in the study of the decomposition of O_2BF_4 is correct, the radicals O_2F may exist for a long time in the gas phase at room temperature. In this connection, it is interesting to note that NF_2, an electronic (but not structural) analogue of O_2F, is stable at temperatures considerably exceeding room temperature, while the radical OOCl, which has the same structure, is unstable in the gas phase.

Exhaustive compilations of the reactions of O_2F_2 investigated up to 1963 have been published[1,93]. This review presents certain data taken from Streng[1,93] and also from later sources.

Dioxygen difluoride does not react with Pyrex glass and quartz. In the recording of the infrared spectrum of O_2F_2, silver chloride and high-pressure polyethylene were employed[70]. Polytetrafluoroethylene apparently reacts with O_2F_2.[74] In contact with platinum, O_2F_2 explodes[1]. The effect of atomic hydrogen at −196°C leads to the substitution of F by H atoms and to the dissociation of the O–O bond in dioxygen difluoride[93]:

$$2\,O_2F_2 + 10\,H = 4\,HF + H_2O_2 + 2\,H_2O\ .$$

At −140°C O_2F_2 does not react with N_2O, oxidises NO to NO_2 and FNO_3 at temperatures between −160°C and −70°C, and forms with nitrogen dioxide an unidentified unstable white solid compound[16]. It converts N_2F_4 into NF_3 at −100°C but at −150°C it does not react with N_2F_4 and N_2F_2.[1] The reaction of O_2F_2 with phosphorus trifluoride[93] at −148°C yields phosphorus pentafluoride and a substance to which the formula $(POF_3)_n$ was attributed. It is quite possible that the postulated polymer $(POF_3)_n$ contained dioxygenyl hexafluorophosphate. Sulphur tetrafluoride reacts vigorously with O_2F_2 at about −140°C:

$$SF_4 + O_2F_2 \rightarrow SF_6 + O_2\ .$$

In the presence of perchloryl fluoride as a solvent, it is possible to obtain an extremely unstable product of the addition of O_2F_2 to sulphur tetrafluoride[93]:

$$O_2F_2 + SF_4 \rightarrow O_2SF_6\ .$$

The reactions of O_2F_2 with chlorine and bromine fluorides have been investigated in detail. In the temperature range between −154°C and −143°C, chlorine monofluoride forms with O_2F_2 a violet compound $(O_2ClF_3)_n$:[93,94]

$$n\,O_2F_2 + n\,ClF \rightarrow (O_2ClF_3)_n\ .$$

Chlorine dioxide trifluoride can be stored for a long time at −78°C. This compound does not contain ions and does not dissociate in hydrogen fluoride solution[95]. Other pathways for the formation of chlorine dioxide trifluoride involve the reaction of O_2F_2 with HCl:[93,95]

$$O_2F_2 + 2\,HCl \rightarrow 2\,HF + O_2 + Cl_2,$$
$$O_2F_2 + Cl_2 \rightarrow 2\,ClF + O_2,$$
$$O_2F_2 + ClF \rightarrow O_2ClF_3,$$

or the photochemical reaction of ClF_3 with oxygen at −78°C:[95,96]

$$ClF_3 + O_2 \xrightarrow{h\nu,\,2537\,Å} O_2ClF_3\ .$$

The unstable compound O_2BrF_5, which decomposes completely into O_2 and BrF_5 at −100°C, was obtained by the reaction of O_2F_2 with bromine trifluoride[93,97]. At about −140°C hydrogen bromide reacts with an excess of O_2F_2:

$$3O_2F_2 + HBr \rightarrow O_2BrF_5 + HF + 2O_2 .$$

At low temperatures iodine pentafluoride does not react with O_2F_2 but at elevated temperatures it is converted into the heptafluoride[93].

XeF_2 has been obtained by the reaction of dioxygen difluoride with xenon at −118°C,[98,99] while elemental fluorine does not react with xenon at room temperatures and above. Some of the reactions of dioxygen difluoride enumerated above constitute the usual type of fluorination; the addition of O_2F_2 molecules to another reactant takes place in the reaction with ClF, BrF_3, or SF_4. The possibility of reactions involving O_2F radicals under mild conditions, where a rapid and uncontrollable decomposition of radicals such as O_2F as well as dioxygen difluoride itself is ruled out, is of considerable interest for preparative inorganic chemistry. The transfer of O_2F radicals is also implied in the reactions of O_2F_2 with Lewis acids—fluoride ion acceptors. Such reactions result in the formation of the O_2^+ cation, which, when combined with the anion of a complex fluorine acid, forms a dioxygenyl salt.

At −183° or −160°C dioxygen difluoride fluorinates sulphur dioxide:

$$SO_2 + O_2F_2 \rightarrow F_2SO_2 + O_2 .$$

Apart from the main product (sulphuryl fluoride), smaller amounts of FSO_2OSO_2F and fluoroperoxysulphuryl fluoride FSO_2OOF are also formed[100,101]. Experiments with the oxygen-17 isotope and by the ^{17}O NMR method showed that the synthesis of FSO_2OOF constitutes a reaction of O_2F_2 with transfer of an O_2F radical. Another example of the transfer of O_2F is the reaction of O_2F_2 with hexafluoropropene[102], which takes place smoothly at −183°C in chlorotrifluoromethane. The reaction results in the formation of a high yield of a mixture of isomers: $CF_3CF(OOF)CF_3$ and $CF_3CF_2CF_2OOF$.

4. Other Oxygen Fluorides: O_3F_2, O_4F_2, O_5F_2, and O_6F_2

a. Trioxygen difluoride. The report[103] of the synthesis of O_3F_2 when a liquid mixture of F_2 and O_2 is irradiated with ultraviolet light was treated sceptically and the possibility of the existence of trioxygen difluoride was not taken seriously until the publication in 1959 of the work of Kirshenbaum and Grosse[54]. The name "ozone fluoride"[54] proposed for O_3F_2 did not become established. Trioxygen difluoride melts at about −189°C and can be supercooled to −196°C. On heating to room temperature, O_3F_2 decomposes completely to fluorine and oxygen, probably with formation of dioxygen difluoride as an intermediate in the thermal decomposition. The activation energy for the decomposition of O_3F_2 in the temperature range between −196° and −157°C was found to be 3.7 kcal mole^{-1}.[54]

The conditions for the synthesis of O_3F_2 and O_2F_2 in an electric discharge differ only by the composition of the initial gas mixture: the $F_2:O_2$ ratio is 2:3 for O_3F_2 compared with 1:1 for O_2F_2. According to Kirshenbaum and Grosse[54], a mixture of two volumes of fluorine and three volumes of oxygen is quantitatively converted into O_3F_2 in a glow discharge, the yield reaching 3–4 g h^{-1}. We may note that the desired product can be by no means always synthesised. As a rule, O_2F_2 is formed in the synthesis of O_3F_2 and the oxygen present in excess of the amount required for the synthesis of O_2F_2 either does not react at all or is converted into ozone.

The ESR spectra of O_2F_2 and O_3F_2 have been found to be identical[77]. The paramagnetic centres in both fluorides are the O_2F radicals. The concentration of free radicals in O_3F_2 specimens is higher by two powers of ten than in dioxygen difluoride specimens and reaches 5–10 mole %. It is believed[77] that such a high concentration of O_2F is caused by the thermal decomposition of O_3F_2.

Investigation of the properties of O_3F_2 by spectroscopic methods gave rise to doubts concerning the individuality of trioxygen difluoride. Different models have been proposed[44,80,81,83] whereby it might be possible to account for the characteristics of the ^{19}F and ^{17}O NMR spectra and the mass spectrum of O_3F_2. Probably it is most correct to regard trioxygen difluoride as a mixture of dioxygen difluoride and tetraoxygen difluoride in equilibrium with O_2F radicals; this has been demonstrated by Solomon and coworkers[80,83].

O_2F_2 has been obtained by the reaction of fluorine activated in a discharge (atomic fluorine) with O_3F_2 at −196°C, i.e. F atoms add to the O_2F radicals present in trioxygen difluoride. O_3F_2 does not react with molecular fluorine at −196°C.[54] The reaction of O_3F_2 with boron trifluoride yields O_2BF_4 with evolution of fluorine[83]. The stoichiometry of the reaction

$$4O_3F_2 + 6BF_3 = 6O_2BF_4 + F_2$$

is consistent with the hypothesis that trioxygen difluoride is a mixture of O_2F_2 and O_4F_2.

b. Tetraoxygen difluoride. O_4F_2 has been obtained in a gas discharge reaction of fluorine and oxygen under mild conditions[55,104]. This compound is probably formed as a result of the recombination of O_2F radicals:

$$FO_2 + O_2F = O_4F_2 ,$$

but other reactions cannot be ruled out[58,64]:

$$O_2F + O_2 \rightarrow O_4F \xrightarrow{+F} O_4F_2,$$
$$F + O_4 \rightarrow O_4F \xrightarrow{+F} O_4F_2 .$$

The O_4F_2 molecule probably consists of the atomic chain F–O–O–O–O–F, where the O–O bonds adjoining the fluorine atoms are equivalent and close in strength to double bonds[64]. The dissociation energy of the central O–O bond hardly exceeds about 3 kcal mole^{-1}.[58] The ESR spectrum of O_4F_2 is determined[105], as for O_2F_2 and O_3F_2, by O_2F radicals. The red-brown solid O_4F_2 melts at −191° ± 2°C and explodes on being heated rapidly. The O_4F_2 vapour pressure is 0.25 mmHg at −183°C.[104] The half life of O_4F_2 at −183°C is 16 days but at −196°C the compound or its solutions in carbon tetrafluoride can be stored for several weeks[104]. The final products of the thermal decomposition of O_4F_2 are fluorine and oxygen. Like O_2F_2, tetraoxygen difluoride forms a dioxygenyl salt with boron trifluoride[83,92]. At −196°C O_4F_2 reacts with tetrafluorohydrazine, forming nitrogen trifluoride[104].

c. Higher representatives of the polyoxygendifluoride family. In 1966 the preparation of oxygen fluorides with the empirical formulae O_5F_2 and O_6F_2 was described[56]. The first compound decomposes slowly at −196°C and rapidly at −183°C, the final decomposition products of O_5F_2 being fluorine and oxygen. The second compound decomposes slowly on heating from −213° to −183°C with evolution of ozone, while rapid heating from −183°C results in an explosion of O_6F_2.

The solubility of O_5F_2 and O_6F_2 in liquid oxygen difluoride is about 5 wt.% at −208° and −213°C respectively. The structures of O_5F_2 and O_6F_2 are unknown. The attempts to obtain fluorides with a higher oxygen content from an initial $5O_2-F_2$ mixture by the method described for the synthesis of O_5F_2 and O_6F_2 were unsuccessful[56]. The preparation of a mixture of oxygen fluorides, one of the components of which might have been O_6F_2, was reported in 1969.[58]

The thermal stability of polyoxygen difluorides decreases with increasing number of oxygen atoms in the O_nF_2 molecule: for $n > 2$, the compounds are extremely unstable or their very existence is debatable. However, CF_3OOF, CF_3OOCF_3, and CF_3OOOCF_3 (and possibly $CF_3OOOOCF_3$), i.e. perfluoroalkyl derivatives of polyoxygen difluorides, exist and are much more stable than the corresponding oxygen fluorides[2]. The increase of the stability of the chain of oxygen atoms is an extremely interesting result of the substitution of fluorine atoms by perfluoroalkyl radicals and merits a more detailed investigation.

III. DIOXYGENYL COMPOUNDS

The existing methods for the synthesis of dioxygenyl compounds consist in the oxidation of molecular oxygen:

$$O_2 + PtF_6 \rightarrow O_2^+PtF_6^-$$

and the reaction of oxygen fluorides (O_2F radicals) with the corresponding Lewis acids:

$$O_2F + BF_3 \rightarrow O_2F \cdot BF_3 \rightarrow O_2^+BF_4^-$$

or

$$O_2F + EF_5 \rightarrow O_2F \cdot EF_5 \rightarrow O_2^+EF_6^- \ (E=P, As, Sb, Bi)$$

1. Dioxygenyl Hexafluoroplatinate

Dioxygenyl hexafluoroplatinate was described in 1962.[4,106] It is formed in the fluorination of platinum or its salts in glass and quartz vessels. The oxygen required for the synthesis of O_2PtF_6 is evolved in this case when fluorine acts on the walls of the reaction vessel. Treatment of platinum sponge with a mixture of fluorine and oxygen at 450°C or heating of platinum sponge in an atmosphere of OF_2 also leads to the synthesis of O_2PtF_6. At room temperature O_2PtF_6 was obtained by tensimetric titration of oxygen with platinum hexafluoride.

The crystal lattice energy of $O_2^+PtF_6^-$ calculated from the Kapustinskii equation is −125 kcal mole^{-1} and the electron affinity of platinum hexafluoride has been estimated as not less than 7 eV. Platinum hexafluoride is a powerful oxidising agent capable of forming crystalline compounds on reaction with molecular oxygen or xenon. However, the attempts to carry out the reaction between PtF_6 and krypton, nitrogen, or nitrogen trifluoride were unsuccessful[107,108].

Dioxygenyl hexafluoroplatinate is a red solid which sublimes above 90°C in a vacuum and melts with decomposition at 219°C.[106] Two modifications of O_2PtF_6 have been established by X-ray diffraction: a rhombohedral low-temperature modification and a high-temperature cubic modification with a unit cell parameter $a = 10.032$ Å and $z = 8$. The $r(O-O) = 1.13$ Å distance obtained in an X-ray diffraction study[106] is not entirely reliable owing to the difficulty of determining the positions of the light O atoms in the presence of the heavy Pt atoms. In a neutron diffraction study[109] of O_2PtF_6 powder, only the limits of $r(O-O)$ were found: 0.9–1.4 Å. The magnetic susceptibility of this compound in the range 88–294°K obeys the Curie–Weiss law. The magnetic moment $\mu_{eff} = 2.57$ Bohr magnetons[106] is close to the pure spin moment for two unpaired electrons (2.83 Bohr magnetons); one unpaired electron belongs to the O_2^+ and the other to the octahedral PtF_6^- ion. The magnetic moment $\mu_{eff}(O_2^+) = 1.57$ Bohr magnetons at room temperature[110]. In the Raman spectrum of O_2PtF_6 the O_2^+ vibration frequency is 1837 cm^{-1}.[108]

Dioxygenyl hexafluoroplatinate reacts vigorously with water, evolving oxygen and a small amount of ozone. The solution formed on hydrolysis contains PtF_6^{2-} ions and the residue consists of hydrated PtO_2. The hydrolysis of O_2PtF_6 by water vapour takes place similarly[4]. The reaction of O_2PtF_6 vapour with heated potassium fluoride or the reaction of potassium fluoride with O_2PtF_6 in iodine pentafluoride leads to the substitution of the O_2^+ cation by K^+. The reactions of O_2PtF_6 with bromine trifluoride and selenium tetrafluoride proceed as follows:

$$O_2PtF_6 + 3BrF_3 \rightarrow (BrF_3)_2PtF_4 + BrF_5 + O_2,$$
$$O_2PtF_6 + 3SeF_4 \rightarrow (SeF_4)_2PtF_4 + SeF_6 + O_2.$$

The reactions of O_2PtF_6 with ClF_3 and IF_5 yielded difluorochlorinium and tetrafluoroiodinium hexafluoroplatinates[4,106]. Dioxygenyl hexafluoroplatinate reacts vigorously with benzene, cyclohexane, and pyridine but not with carbon tetrachloride.

2. Dioxygenyl Compounds of Group V Elements

The synthesis of salts with the general formula O_2EF_6 (E = P, As, or Sb) was reported in 1964.[111,112] In addition a patent[113] taken out by Young et al.[111] reports the bismuth compound O_2BiF_6. The method of synthesis of the compound O_2EF_6 is based on the reaction of dioxygen difluoride with fluorine-containing Lewis acids—the pentafluorides of Group V elements. The synthesis is carried out at a low temperature by bringing dioxygen difluoride and the condensed pentafluoride into contact, either directly in a discharge reactor where O_2F_2 is obtained or O_2F_2 is distilled into a separate trap containing the other reactant. The end of reaction is indicated by the disappearance of the orange colour of dioxygen difluoride. The solid reaction products are kept for several hours in a vacuum to remove the excess pentafluoride. The dioxygenyl salts of arsenic and antimony are also obtained when daylight is allowed to act on a mixture of oxygen, fluorine, and arsenic or antimony pentafluoride[59]. A thermal synthesis of dioxygenyl compounds was described in 1969.[41] When mixtures of OF_2 and AsF_5 are heated to 200°C and a pressure of 200 atm, dioxygenyl hexafluoroarsenate is formed in a yield up to 80%: $4OF_2 + 2AsF_5 = 2O_2AsF_6 + 3F_2$. A mixture of fluorine and oxygen may be used instead of oxygen difluoride. O_2AsF_6 has been obtained in almost quantitative yield by heating the starting materials in the proportions $F_2 : O_2 : AsF_5 = 1 : 2 : 2$ at 130°C or 200°C and 150 atm for 5–7 days. Similar results were achieved in experiments using antimony pentafluoride as the Lewis acid. The attempts to obtain dioxygenyl salts by this method from BF_3, PF_5, SiF_4, BrF_3, BrF_5, and IF_5 were unsuccessful[41].

a. Dioxygenyl hexafluorophosphate. When O_2PF_6 is prepared by the reaction

$$O_2F_2 + PF_5 \xrightarrow{-126 \text{ or } -100^\circ} O_2PF_6 + {}^1/_2F_2,$$

a certain amount of POF_3 is formed. The solid white dioxygenyl hexafluorophosphate is a very unstable compound which decomposes slowly at −80°C.[111-113]. At room temperature O_2PF_6 decomposes rapidly:

$$O_2PF_6 \rightarrow O_2 + {}^1/_2F_2 + PF_5.$$

Owing to its low thermal stability, O_2PF_6 is not formed when fluorine, oxygen, and PF_5 are heated together[41].

The reaction of O_2PF_6 with water leads to the evolution of oxygen; O_2PF_6 reacts with nitrogen dioxide according to the equation[111]

$$O_2PF_6 + NO_2 = O_2 + NO_2PF_6.$$

b. Dioxygenyl hexafluoroarsenate. Apart from the methods for the preparation of O_2PF_6 enumerated above, the reaction of fluorodiazonium hexafluoroarsenate with oxygen has been mentioned[16]:

$$N_2FAsF_6 + O_2 \xrightarrow{2 \text{ atm}} O_2AsF_6 + N_2 + {}^1/_2F_2.$$

Dioxygenyl hexafluoroarsenate is stable below 100°C but decomposes rapidly at 130–180°C:[111]

$$O_2AsF_6 = O_2 + {}^1/_2F_2 + AsF_5.$$

The O_2^+ peak has been recorded in the mass spectrum of the vapour over a specimen of pure O_2AsF_6 at a pressure of the order of 10^{-6} mmHg and room temperature[111]. X-Ray powder diffraction patterns of O_2AsF_6 and $NOAsF_6$ show that these compounds are isomorphous, which confirms the ionic structure $O_2^+AsF_6^-$. The unit cell parameter of the cubic O_2AsF_6 lattice is $a = 8.00$ Å [111] or 8.10 Å.[59] The infrared spectrum of dioxygenyl hexafluoroarsenate contains a single absorption band at 705 cm^{-1}, which is characteristic of the AsF_6^- ion[41,59,111]. The vibrations of the octahedral AsF_6^- ion at 688, 574, and 375 cm^{-1} and the vibration of the O_2^+ ion at 1858 cm^{-1} are active in the Raman spectrum[114] of O_2AsF_6. A singlet line with a g-factor of 1.9980 has been observed in the ESR spectrum of dioxygenyl hexafluoroarsenate.

The hydrolysis of O_2AsF_6 is described by the equation

$$2\,O_2AsF_6 + H_2O = O_2 + O_3 + HAsF_6,$$

and its reaction with nitrogen dioxide yields a nitronium salt[111].

b. Dioxygenyl fluoroantimonates. In general the reaction between dioxygen difluoride and SbF_5 cannot be described by the equation $O_2F_2 + EF_5 = O_2EF_6 + \frac{1}{2}F_2$ (E = Sb), which is valid for phosphorus and antimony pentafluorides. In contrast to arsenic pentafluoride, SbF_5 is considerably associated and contains fluorine bridge bonds. The existence of polymeric (dimeric and trimeric) fluoroantimonate anions is well known, for example in the compounds $N_2F_3^+Sb_2F_{11}^-$ [115] and $ClO_2^+Sb_3F_{16}^-$ [116] (incidentally, arsenic pentafluoride also forms the dimeric ions $As_2F_{11}^-$)[117]. SbF_5 probably reacts in the monomeric form at an elevated temperature[41]. The composition of the product of the low-temperature reaction of dioxygen difluoride and antimony pentafluoride corresponds more closely to the compound $O_2Sb_2F_{11}$ than to O_2SbF_6.[118] The authors of an early investigation[111] probably synthesised $O_2Sb_2F_{11}$ from dioxygen difluoride and antimony pentafluoride. Little is known about the interaction of antimony trifluoride with dioxygen difluoride; it has only been reported that O_2SbF_6 could not be obtained by the reaction of SbF_3 with O_2F_2.[16]

The face-centred cubic unit cell of O_2SbF_6 is a = 10.13 Å [41] or a = 10.30 Å.[59] Nikitina and Rosolovskii[118] found a = 5.07 Å (z = 1) for the cubic O_2SbF_6 lattice. The compound $O_2Sb_2F_{11}$ is usually amorphous to X-rays; certain specimens give rise to an X-ray diffraction pattern with two intense lines (d = 3.95 and 3.59 Å), the number of lines increasing after fusion of the salt[118]. The infrared spectrum of O_2SbF_6 contains the ~669 cm^{-1} band of the SbF_6^- anion[41,118]. The fluoroantimonate $O_2Sb_2F_{11}$ absorbs at 492 and 665–715 cm^{-1}; it is suggested that the absorption at 492 cm^{-1} is caused by the vibrations of the Sb–F–Sb bridge bond[118]. The O_2^+ vibration is observed in the Raman spectrum of solid O_2SbF_6 at 1862 cm^{-1} or at 1860 cm^{-1} for an O_2SbF_6 solution in SbF_5.[114] The magnetic susceptibility of O_2SbF_6 has been measured in the range 80–333°K.[119] The effective magnetic moment at room temperature is 1.65 Bohr magnetons.

Dioxygenyl fluoroantimonates have been investigated by differential thermal analysis[118]. The endothermic effect in the thermogram of $O_2Sb_2F_{11}$ at 180–185°C corresponds to its fusion, rapid decomposition beginning above 260°C. The thermogram of O_2SbF_6 shows three endothermic effects: at 160–165°C (polymorphic transformation), 240–245°C (decomposition), and about 280°C. The two-stage decomposition process of O_2SbF_6 involves the mechanism

$$2\,O_2SbF_6 \xrightarrow{\sim 240^\circ} O_2 + {}^1/_2F_2 + O_2Sb_2F_{11},$$

$$O_2Sb_2F_{11} \xrightarrow{\sim 280^\circ} O_2 + {}^1/_2F_2 + 2SbF_5.$$

Thus dioxygenyl fluoroantimonates are much more stable to heat than dioxygenyl fluorophosphate and fluoroarsenate. On heating in a vacuum above 130°C, $O_2Sb_2F_{11}$ is converted into O_2SbF_6:

$$O_2Sb_2F_{11} \rightarrow O_2SbF_6 + SbF_5.$$

By heating a mixture of $O_2Sb_2F_6$ and antimony pentafluoride at 180–200°C, it is possible to obtain $O_2Sb_2F_{11}$, i.e. we have the equilibrium

$$O_2Sb_2F_{11} \rightleftharpoons O_2SbF_6 + SbF_5.$$

which is almost completely displaced to the left at room temperature[118].

3. Dioxygenyl Tetrafluoroborate

Dioxygenyl tetrafluoroborate was apparently obtained in 1960 from boron trifluoride, oxygen, and fluorine in a glow discharge[16]. In 1964 the synthesis of O_2BF_4 by the reaction of dioxygen difluoride with boron trifluoride at −126°C was reported[112]. Subsequently[83,92] the reaction of O_4F_2 with BF_3 was investigated: $\frac{1}{2}O_4F_2 + BF_3 = O_2BF_4$. It was established[92] that at −138°C O_4F_2 reacts with BF_3 much more vigorously than does O_2F_2 at −126°C. The difference between the reaction rates can be readily accounted for: O_4F_2 apparently dissociates more readily into O_2F radicals than does O_2F_2, but this difference is not fundamental since it has been shown[58] that the reaction of several millimoles of BF_3 with dioxygen difluoride at −126°C terminates in 10 min, which is comparable to the rate of reaction between O_4F_2 and BF_3.[92] It is known[58] that O_2BF_4 is formed when bremsstrahlung with an energy of 3 MeV acts upon a mixture of BF_3, O_2, and F_2 in a sapphire reactor.

X-Ray powder diffraction patterns of O_2BF_4 and $NOBF_4$ show that these compounds are isomorphous. The orthorhombic unit cell of O_2BF_4 has the parameters a = 8.77 Å, b = 5.58 Å, and c = 7.05 Å.[58] The effective

magnetic moment of O_2BF_4 is 1.7 Bohr magnetons[120]. The unpaired electron of the cation has been detected by ESR spectroscopy[58,112]. The vibrations of the BF_4^- ion have been found in the infrared spectrum[121] of O_2BF_4 recorded at −196°C at the following frequencies (cm^{-1}): 769 (ν_1), 374, 362 (ν_2), a broad band at 1200–900 (ν_3), 532, 518 (ν_4). The ν_1 and ν_2 vibrations of the free tetrahedral (T_d) BF_4^- ion are inactive in the infrared spectrum. The appearance of these frequencies in the O_2BF_4 spectrum can be explained by a decrease of the symmetry of the BF_4^- ion. The O_2^+ vibration gives rise to a weak doublet in the infrared spectrum of O_2BF_4 at 1868 and 1866 cm^{-1}. The substitution of the oxygen-16 isotope by oxygen-18 leads to a shift of the doublet to 1764 and 1762 cm^{-1}. The splitting of the O_2^+ band is caused by interionic interactions in the unit cell of the crystal. The vibration frequencies of the O_2^+ ions and dioxygenyl compounds are close to that of the free ion at 1876 cm^{-1}, which confirms the existence of O_2^+ in the salts.

Reactions involving the formation and decomposition of O_2BF_4 have been investigated by the tracer atom method[92] using radioactive fluorine-18. The salt decomposes slowly at 0°C and comparatively rapidly at room temperature. O_2BF_4 specimens decompose completely in several hours in a "dynamic" vacuum but in a sealed vessel the decomposition is only partial over a period of several weeks[92]. This behaviour can be accounted for by the equilibrium

$$O_2BF_4(\text{solid}) \rightleftharpoons O_2F(\text{gas}) + BF_3(\text{gas}). \qquad (***)$$

Boron trifluoride suppresses the dissociation of O_2BF_4. Fluorine and oxygen are formed in the decomposition of O_2BF_4 by the dimolecular reaction

$$O_2F + O_2F \xrightarrow{k} F_2 + 2O_2.$$

In the experimental temperature range 0–32°C the decomposition of O_2BF_4 is described by the equation[92]

$$dp_{BF_3}/dt = kK^2/p^2_{BF_3},$$

where K is the equilibrium constant of reaction (***).

Like the dioxygenyl salts already examined, O_2BF_4 reacts with nitrogen dioxide and is hydrolysed with evolution of ozone[112]. Dioxygenyl tetrafluoroborate reacts vigorously with organic solvents but dissolves in cyanogen without reaction at −25°C.[58] Certain chemical properties of O_2BF_4 have been described by Goetschel et al.[122] When O_2BF_4 reacts with substances the ionisation potential of which is lower than that of oxygen, O_2^+ is reduced and a fluoroborate with another cation is formed. If the resulting fluoroborate is unstable, BF_3 and fluorine are evolved, i.e. O_2BF_4 can behave as a fluorinating agent. For example, O_2BF_4 reacts smoothly at −25°C with carbon tetrachloride, forming $CFCl_3$ and CF_2Cl_2. The reaction of O_2BF_4 with hexafluorobenzene yields a mixture of fluorocarbons; saturated fluorocarbons do not react with O_2BF_4. The reaction of O_2BF_4 with xenon, accompanied by evolution of O_2, takes place rapidly at −96°C and it is believed that it involves the formation of $XeBF_4$. Oxygen is evolved in the reaction of O_2BF_4 with ClO_4, Cl_2, and ClF_3. Chloryl tetrafluoroborate has been obtained by the reaction of O_2BF_4 with ClO_2.

The reaction of BF_3 with a mixture of oxygen fluorides obtained by the radiolysis of F_2 and O_2 probably results in the formation of the unstable O_6BF_4 and O_4BF_4 in addition to O_2BF_4:[58]

$$O_6F + BF_3 = O_6BF_4 \text{ (decomposes at } -140°),$$
$$O_4F + BF_3 = O_4BF_4 \text{ (decomposes at } -33°).$$

However, reliable evidence for the existence of these interesting compounds has not so far been obtained.

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Dioxygenyl fluoro-complexes are formed by a few higher fluorides of the elements: BF_3, PF_5, AsF_5, SbF_5, BiF_5, PtF_6, and possibly SnF_4,[123] and also VF_5.[124] The stabilisation of the O_2^+ cation, i.e. the shift of the equilibrium $O_2 + X \rightleftharpoons O_2^+ + X^-$ to the right, depends significantly on the nature of X. Platinum hexafluoride, the most powerful electron acceptor, readily oxidises molecular oxygen. The Lewis acids BF_3 and EF_5 do not react with molecular oxygen but do react with O_2F radicals, which constitute a kind of "precursor" containing "almost" molecular oxygen, i.e. two oxygen atoms linked almost as strongly as in the O_2 molecule:

$$O_2F + EF_5(BF_3) \rightarrow O_2F \cdot EF_5(BF_3).$$

In this stage of the reaction, the polarisation of the O–F bond probably increases and the tendency towards the formation of a stable tetrahedral or octahedral anion induces a transfer of F^- to the environment of the central atom in the Lewis acid:

$$O_2F \cdot EF_5(BF_3) \rightarrow O_2^+EF_6^-(BF_4^-).$$

All the known dioxygenyl salts are oxidising agents, the chemical properties of which have not been investigated in sufficient detail.

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Kinetics and Nature of Mechanochemical Reactions

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Certain general characteristics of the kinetics, mechanism, and nature of the primary step in chemical reactions initiated by mechanical action in various low- and high-molecular-weight substances have been examined. The formal kinetics of mechanochemical reactions occurring in constant and variable mechanical fields have been analysed in Section II. In constant fields the rate of the process is determined by the rate of the primary chemical stage and in variable fields the rate-limiting stage may be the supply and absorption of elastic energy. Section III deals with the mechanisms of the conversion of elastic into chemical energy. The chemical changes in a substance are associated either with the elastic deformation of the electron shells of the reacting species or with the generation of non-equilibrium vibrationally excited states in the process of dissipation of elastic energy as heat. Under certain conditions, local short-lived regions of intense absorption of elastic energy may play a major role. Data concerning the nature of the primary active species in mechanochemical reactions —free radicals in various charged states—are discussed in the last section.
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I. INTRODUCTION

The studies in various fields of mechanochemistry are widely scattered. The mechanochemistry of polymers [1-9] is separated from studies on mechanochemical reactions in solids (the German term is tribochemical reactions)[10-16]; reactions initiated by ultrasonic waves [17-22], chemical reactions in solids at high pressures with shear stress[23-27], reactions in shock waves [28,29], the phenomenon of detonation on impact [30,31], corrosion under stress [32-34], cryogenic processes [35-37], etc. occupy a special place. All these fields have not been combined into a single discipline and one can only hope that ten years hence mechanochemistry, the science of the initiation and acceleration of chemical reactions in gases, liquids, and solids under the action of elastic energy, will be treated uniformly as part of the field of non-thermal chemical reactions together with radiation chemistry, photochemistry, and other processes.

One may suppose that, despite the historic separation of individual branches of mechanochemistry and despite the differences in the methods used to create mechanical fields and the differences in physicomechanical properties of low- and high-molecular-weight substances in various phase states, there exist common characteristics in the thermodynamics, kinetics, and the nature of the primary step in many classes of mechanochemical reactions. In this review an attempt has been made to isolate, using the simplest and most thoroughly investigated reactions, certain characteristic features of the kinetics and mechanisms of mechanochemical reactions. The main examples have been taken from the mechanochemistry of polymers: in linear macromolecular systems it is simpler to analyse the specific features of the phenomenon; extension to three-dimensional systems probably does not involve fundamental changes in the mechanism of the processes.

II. FORMAL KINETICS OF MECHANOCHEMICAL REACTIONS

Usually the primary data on the mechanisms of chemical reactions are obtained in kinetic studies, for example, in measurement of the variation of the reaction rate constant with temperature, concentration, and other parameters. In radiation chemistry the rate of reaction is not understood as the change of concentration per unit time but as the change of concentration as the result of the absorption of a specified energy dose (the energy yield G is the number of species which have reacted after absorption of 100 eV of energy) and the principal parameters are the dose and the dose rate of the radiation. Similarly in photochemistry the quantum yield of the reaction is primarily determined.

Unfortunately in mechanochemistry an equally clear-cut energy approach has not been developed and energy estimates are encountered extremely rarely. This is associated in the first place with methodological difficulties in measuring the amount of mechanical energy absorbed and also with the indeterminacy of the stresses which actually operate and in the second place with the lack of clear concepts concerning the nature of mechanochemical reactions. As a rule, the appearance of hypotheses about the mechanism of a particular process is accompanied by the simultaneous development of an energy approach in the analysis of its kinetics (a good example of this is ultrasonic chemistry) [38-40].

Mechanochemical reactions constitute a complex multistage process, which include stages involving mechanical deformation of a substance (the supply and absorption of mechanical energy), the primary chemical reaction proper, and various secondary processes. In the kinetics of mechanochemical reactions it is possible to isolate two limiting cases: the first corresponds to conditions under which the rate of the entire process is determined by the rate of the primary mechanochemical stage and in the second the rate-limiting stage is the supply or absorption of mechanical energy. Thus the ratio of the rates of absorption of elastic energy and of the mechanochemical reaction proper constitutes a criterion for the subdivision of mechanochemical processes into two types (based on their kinetics).

1. Kinetics in Constant Mechanical Fields

The first case may obtain under conditions where the substance is in a constant field of mechanical stresses.

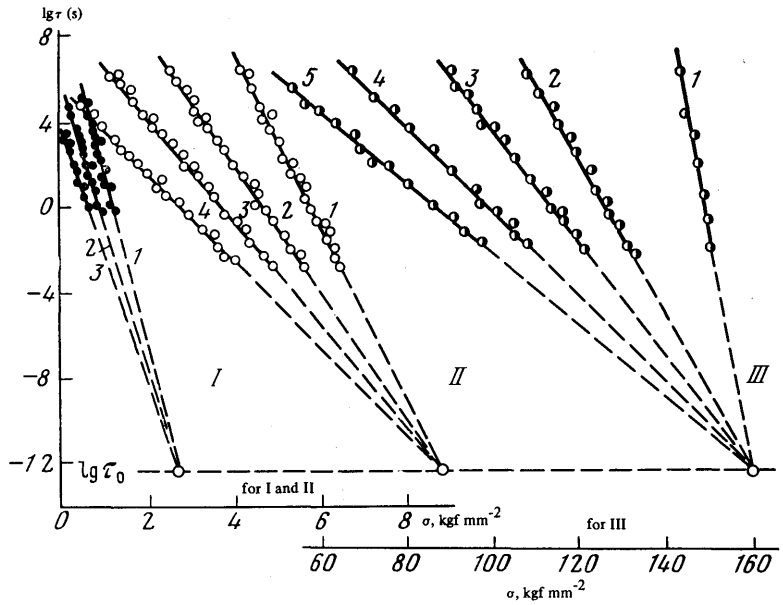

Figure 1. Temperature and time variation of tensile strength: I) rock salt [1) 400°C; 2) 500°C; 3) 600°C]; II) polycrystalline aluminium [1) 18°C; 2) 100°C; 3) 200°C; 4) 300°C]; III) Kapron fibre [1) −180°C; 2) −120°C; 3) −75°C; 4) +20°C; 5) +80°C].

When a constant load is applied, elastic energy is absorbed rapidly and the stage involving elastic deformation may be resolved in time from subsequent slower chemical reactions. Under such conditions, the rate of the mechanochemical process should be determined by the rate of the primary chemical reaction initiated by elastic stresses and the variation of the rate constant with external parameters should reflect the characteristics of this primary reaction.

An example of a process of this type may be degradation of macromolecules on monoaxial extension of polymeric films or fibres by the application of a constant stress. According to the kinetic concept of strength[8], the breakdown of the specimen occurs as a result of the dissociation of mechanically strained macromolecules.

In the idealised case of a uniform distribution of stresses throughout the specimen (under the condition σ = const.), the number of chains bearing the load will decrease with time according to the law

$$N \simeq N_0 \exp(-k_{\text{mech}}\tau). \qquad (1)$$

Here it is assumed that the rate of dissociation of the strained bonds is described by an equation for first-order kinetics (see, for example, Tobolsky and Eyring[41]) and k_{mech} is the rate constant for the mechanical dissociation of polymeric chains. Catastrophic breakdown of the specimen begins when $k_{\text{mech}}\tau = 1$, i.e. the time up to the rupture or, what amounts to the same thing, the lifetime of the specimen τ_{life} is inversely proportional to the rate constant k_{mech}. In other words, the time up to the rupture of the specimen coincides with the characteristic time of the reaction involving the breakdown of the strained polymeric chains and measurements of the lifetime under various stress conditions (medium, temperature, the stress itself, etc.) should in principle throw light on the nature of the primary mechanochemical step.

The formulation of Eqn. (1) only reveals the possibility of a relation between the lifetime and the rate constant for the mechanical dissociation of bonds. A rigorous kinetic theory, which is now being developed, should take into account many aspects of the phenomenon: the structural inhomogeneity of the material and the form of the distribution functions for the stresses throughout its bulk, the variation of the rate constant with the degree of polymerisation and with the magnitude of the effective stresses, secondary free-radical reactions, and the probability of a chain propagation of degradation, etc.

Fig. 1 presents[8] the results of measurements of the variation of the lifetime ($\tau_{\text{life}} \propto 1/k_{\text{mech}}$) of three materials—rock salt, polycrystalline aluminium, and Kapron† fibre with stress (monoaxial extension at σ = const.) at different temperatures. For each material, the $\tau_{\text{life}} = f(T, \sigma)$ relation obeys the Zhurkov equation[42] over a fairly wide range of temperatures T and stresses σ:

$$\tau_{\text{life}} = \tau_0 \exp\left(\frac{U_0 - \gamma\sigma}{RT}\right). \qquad (2)$$

where R is the gas constant and τ_0, U_0, and γ are constants for the given material; γ depends on the nature and history of the specimen and is called the structural factor. The constant τ_0 is always close to magnitude to the vibration period of the atoms in the crystals (about 10^{-13} s). Table 1 presents[8] the results of the calculation of the constant U_0 from measurements of the lifetime at σ = const. and includes for comparison the corresponding values of E—the heats of sublimation of metals or the

†A type of nylon produced in the USSR (Ed. of Translation).

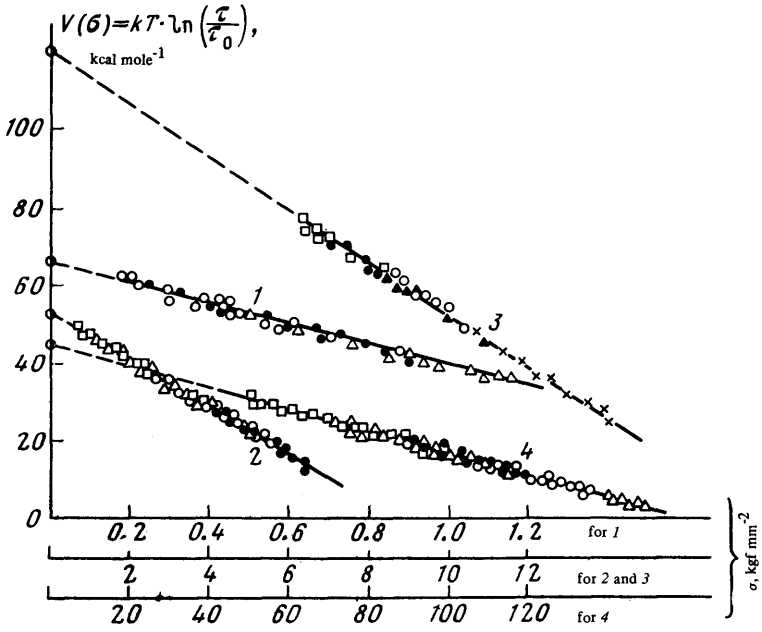

Figure 2. Variation of the effective energy barrier $U = RT\ln(\tau_{life}/\tau_0)$ with tensile stress σ: 1) rock salt; 2) polycrystalline aluminium; 3) polycrystalline platinum; 4) Kapron fibre.

activation energies for the thermal degradation of polymers. A graphical determination of the constant U_0 is illustrated by the data in Fig. 2. [8] To a first approximation, U_0 does not differ markedly from the energy of interatomic bonds.

Table 1. Comparison of the constants U_0 with the heats of sublimation of metals and the activation energies for the thermal degradation of polymers [8].

Substance	U_0, kcal mole^{-1}	E, kcal mole^{-1}
Platinum	120	127
Iron	100	97
Copper	81	80
Aluminium	53	55
Zinc	30	31
Rock salt	68	–
Polytetrafluoroethylene	75	76
Polypropylene	56	58
Kapron	45	43
Poly(vinyl chloride)	35	32

The agreement of τ_0 and U_0 with molecular constants confirms the hypothesis that the kinetic behaviour of mechanochemical processes in constant mechanical fields are indeed determined by the characteristics of the primary chemical reaction stage.

Reactions in constant mechanical fields include also the electrochemical dissolution of metals under the simultaneous influence of mechanical stresses (corrosion under stress) [32-34,43-45]. In this case measurements are made of the so called polarisation diagrams: the variation of the anodic (or cathodic) current i with the electrical potential φ. [43] In the absence of mechanical stresses, these values are related as follows:

$$i = K_{el}\exp\left(\frac{\alpha\varphi - \varphi^0}{b}\right), \qquad (3)$$

where K_{el} is a constant, φ^0 the standard electrode potential of the metal, $b = RT/zF$, z is the valency of the ion, and F the Faraday.

Line *1* in Fig. 3*a* illustrates [43] this relation in terms of a plot of φ against $\lg i$. In a mechanically deformed metal the linear relation between φ and $\lg i$ persists, but, over a certain range of stresses, the corresponding straight lines are displaced upwards to an extent which is greater for increasing relative deformation. The data in Fig. 3*b* illustrate [44] the relation between the mechanochemical effect (the variation of the corrosion current—curve *2*) with increase in strength on deformation. Evidently, in the stage involving an intense increase in strength on deformation (region *E*), the effect increases and in the concluding stage, when the planar accumulations of dislocations break down, the effect diminishes [34].

Thus, in the stage involving an increase in strength (region *E*), the metal "becomes less noble" under the influence of mechanical stresses—the standard potential φ^0 diminishes by an amount $\Delta\varphi^0$, which depends on the degree of increase in strength $\Delta\sigma$ due to deformation ($\Delta\sigma$ is the amount by which the stress applied to the material exceeds the microscopic yield point). According to the literature [34,35],

$$\Delta\varphi^0 = -\frac{nR}{\bar{\alpha}R'ZF}\Delta\sigma,$$

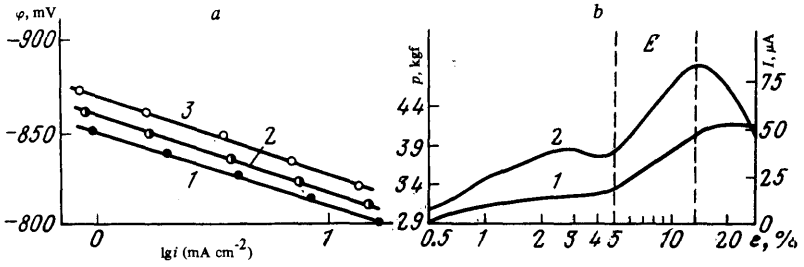

Figure 3. Kinetics of corrosion under stress: *a*) variation of the anodic current with electrical potential for steel 20 in 1.1 *N* sulphuric acid at 20 (°C ?) [degree of deformation (%): 1) 0; 2) 10; 3) 30]; *b*) variation of the corrosion current (curve *2*) and the extending force (curve *1*) with the degree of deformation; 08SV steel in 7 *N* sulphuric acid solution; rate of extension 34% per minute.

where n is the number of coplanar dislocations in planar accumulations, $\bar{\alpha}$ the coefficient in the equation relating the density of dislocations to the degree of deformation of the metal, $R' = kN_{max}$, k is the Boltzmann constant, and N_{max} the maximum possible density of dislocations (in metals $N_{max} \simeq 10^{12}$ cm^{-2}). The general equation for the kinetics of electrochemical or chemical dissolution of a metal under the simultaneous influence of mechanical stresses is of the form

$$i = K_{\text{electrochem}} \exp\left(\frac{A}{RT} + \frac{n\Delta\sigma}{\bar{\alpha}R'T}\right), \qquad (4)$$

where A is chemical or electrochemical affinity. The second term in the exponent reflects the effect of mechanical stresses on the chemical potential of the metal, which determines the rate of the process in a constant mechanical field.

2. Reactions in Variable Mechanical Fields

The second limiting case of the kinetics of mechanochemical processes [9,46] corresponds to conditions under which the rate of supply or absorption of elastic energy is much less than the rate of reaction initiated as a result of the absorption of this energy. Such conditions may obtain, for example, under the influence of periodic stress application at frequencies in the range of the intrinsic mechanical losses of the material. This may occur in various types of fatigue tests, under the influence of ultrasonic waves on polymer solutions, in the comminution of solids in mills, in the breakdown of the surface layer of materials on friction, etc.

When the material is acted upon in cyclic processes under steady-state conditions, the time-average mechanical power supplied to the specimen remains constant. In each single stress-application cycle part of the mechanical energy is absorbed by the material and after a certain number of cycles an average steady-state degree of deformation of the material and a corresponding average level of absorbed energy ΔE_{def} are established. The rate of absorption of energy is directly proportional to the power supplied W and the rate of dissipation is equal to the average level ΔE_{def}. Under steady-state conditions,

$$\alpha W = \frac{1}{\tau_r}\Delta E_{def} \quad \text{or} \quad \Delta E_{def} = \alpha\tau_r W \qquad (5)$$

where α is a coefficient the value of which is close to the mechanochemical efficiency of the process (efficiency $< \alpha < 1$) and τ_r is the relaxation time of the stresses.

Real materials are inhomogeneous and the deformation energy is non-uniformly distributed among the system of bonds: the form of the distribution function is in general unknown. To make the treatment concrete, one may suppose that the distribution is fairly steep and is described by an exponential law, i.e. the fraction of bonds characterised by a deformation energy E_{def} and above is proportional to $\exp(-E_{def}/\Delta E_{def})$. Moreover, since the stresses operate periodically, there is a constant redistribution of energy in the system with a characteristic time $1/A$, which depends both on the frequency of application of mechanical action and on the intrinsic relaxation time of the material.

When the rate of the mechanochemical process is limited by the redistribution of mechanical energy in the system, the rate constant should be proportional to the rate of redistribution of deformation energy among the bonds (A, s^{-1}) and the probability of the accumulation at a given bond of a certain critical deformation energy E^*_{def} sufficient to initiate the mechanical reaction. Therefore, considering Eqn. (5), [46] we then have

$$k_{\text{mech}} \simeq A \exp\left(-\frac{E^*_{def}}{\alpha\tau_r W}\right), \qquad (6)$$

Outwardly Eqn. (6) resembles the Arrhenius equation for the variation of the unimolecular decomposition rate constant with temperature, but the significance of the constants is in this case quite different. The pre-exponential factor in Eqn. (6) should be close in magnitude to the rates of relaxation of stresses and not to the vibration frequencies of atoms (10^{12}–10^{13} s^{-1}). The temperature in the exponent in Eqn. (6) is replaced by the rate of supply of mechanical energy. One must stipulate that the distribution function of stresses may also have a different form with a corresponding change in the form of Eqn. (6).

The variation of the rate constant for a mechanochemical reaction with the rate of supply of mechanical energy in variable fields has been measured (Fig. 4) [40,46] in several cases: in ultrasonic degradation of polystyrene in dilute solutions [40], in the comminution of poly(methyl methacrylate) in a vibration mill [46], and in dynamic tests on vulcanised rubbers [47]. In the first two cases the range of rates is very wide (W changes by a factor of 20,

which is much more than usually happens in measurements of the activation energies for thermal reactions where the temperature changes at most by a factor of 2–3).

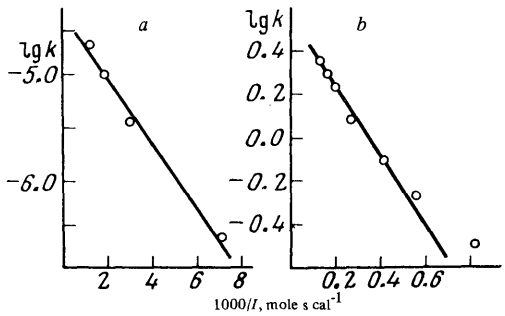

Figure 4. Variation of the rate constant for mechanical degradation with the rate of supply of mechanical energy (lg k plotted against $1000/I$): *a*) comminution of poly(methyl methacrylate) in a vibration mill; *b*) ultrasonic degradation of polystyrene.

Very low values of the pre-exponential factor (10^1–10^{-4} s^{-1}) were obtained throughout (Table 2). This confirms the hypothesis that the rate of the process is indeed limited by the rate of redistribution of elastic energy in the system, i.e. by the physicomechanical properties of the material. Unfortunately the constants α and τ_r are unknown and therefore E^*_{def}, i.e. the minimum deformation energy necessary to initiate the reaction, cannot be determined. To estimate the order of magnitude of the constant τ_r, one may suppose that $\alpha \simeq 10^{-2}$ (this is confirmed by the energy yields for degradation) and $10^4 < E^*_{def} < 10^5$ cal mole^{-1}. Then we have for poly(methyl methacrylate):

$$\frac{E^*_{def}}{\alpha\tau_r} = 700 \text{ or } \tau_r = \frac{10^4 - 10^5}{700 \cdot 10^{-2}} \simeq 10^3 - 10^4 \text{ s}^{-1}.$$

As was to be expected, the relaxation time τ_r and the constant $1/A$ are of a similar order of magnitude.

Table 2. The constants A and $E^*_{def}/\alpha\tau_r$ in Eqn. (6) for various materials.

Material	Conditions of measurements	A, s^{-1}	$E^*_{def}/\alpha\tau_r$	Refs.
Poly(methyl methacrylate)	Dispersion in vibration mill	10^{-4}	70	46
Polystyrene	Ultrasonic degradation in solution	3÷5	3700	40
Vulcanised rubber	Dynamic tests	10^{-2}	—	48

Eqn. (6) has several important consequences. Firstly, in variable mechanical fields the efficiency of the mechanochemical process should increase sharply with the intensity of mechanical action, the conditions of maximum concentration of mechanical energy per unit volume of the substance and per unit time being the most favourable. When the intensity is low, the characteristic effects associated with the contribution by non-relaxed stresses (the ΔE_{def} level) may not appear at all.

Secondly, in mechanochemical processes in variable fields, the frequency of application of mechanical action plays a major role. Thus in the mechanical degradation of poly(methyl methacrylate) in a vibration mill, $\tau_r \simeq 10^3$ to 10^4 s. Consequently, when the process is interrupted for a period of this duration, the rate of the mechanochemical reaction should fall appreciably. Fig. 5 presents [46] results of the measurements of the rate of degradation of poly(methyl methacrylate) under two types of conditions: continuous and periodic (duration of interruption 300 s). In degradation with interruptions the rate of bond dissociation fell almost by a factor of 2.

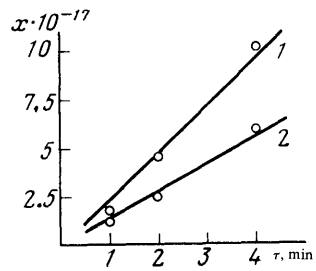

Figure 5. Mechanical degradation of poly(methyl methacrylate) in a vibration mill (x = number of bonds dissociated; temperature 100°K): 1) continuous conditions; 2) periodic conditions (5 min interruptions).

In solids the frequency of application of mechanical action should probably fall within the limits of the frequency spectrum of mechanical losses, including the low-frequency region (see, for example, Fitzgerald [49]). For mechanochemical reactions in gases, it is important that the frequency should correspond to the relaxation time for the transmission of energy from translational to vibrational degrees of freedom of molecules (the phenomenon of the dispersion of sound in gases [17]).

The temperature variation of the rate of a mechanochemical reaction is not explicitly included in Eqn. (6), but the constants of this equation, related to the relaxation times of the stresses, depend on temperature. For example, in polymers they should change sharply in the region of structural transitions, primarily near the glass temperature T_g. Therefore one may expect that, for degradation in variable mechanical fields, the form of the temperature variation of the rate of degradation will alter as T_g is approached. We may note for comparison that under static conditions (constant mechanical fields), when the rate constant for degradation is determined by the molecular constants τ_0 and U_0, the temperature variation of the rate of degradation of polymers does not change near T_g (see, for example, Fig. 1).

Polukhina and Baramboim [51] measured simultaneously the rate of mechanical degradation (comminution of polymers in a vibration mill) and the modulus of elasticity (the rate of propagation of longitudinal sonic waves C_e).

The relation between k_{mech} and C_e for polystyrene, poly(methyl methacrylate), and poly(vinyl acetate) in the temperature range 223–303°K is presented in Fig. 6.[51] Below T_g ($10^{-6}C_e$ cm $s^{-1} > 15$), the points corresponding to the three different polymers fit satisfactorily on a common section of line A. Above the glass temperature ($10^{-6}C_e$ cm^{-1} $s^{-1} < 10$) the nature of this relation changes sharply (straight line *B*). These data confirm yet again the hypothesis that in variable mechanical fields the rate of a mechanochemical reaction and the temperature variation of k_{mech} are closely related to the physicomechanical properties of the substance, i.e. the rate-limiting stage is the redistribution of elastic energy.

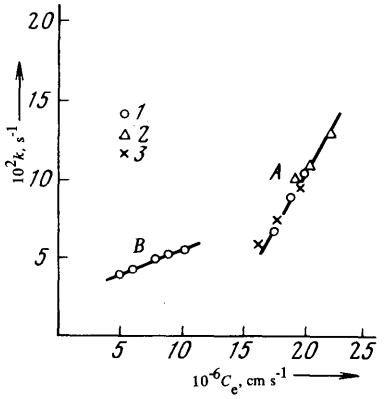

Figure 6. Relation between the rate constant for the mechanical degradation of polymers and the rate of propagation of longitudinal sonic waves C_e in the temperature range 223–303°K; polymer: 1) poly(vinyl acetate); 2) polystyrene; 3) poly(methyl methacrylate).

3. Characteristics of the Kinetics of Reactions in Polydisperse Systems

The conclusions concerning the rate-limiting stages in the kinetics of mechanochemical reactions are probably valid for a wide range of processes in both low- and high-molecular-weight systems. Eqns. (2), (4), and (6) explain the nature of the rate constant. However, frequently the rate constant for a mechanochemical reaction does not remain constant during the mechanical treatment of the substance. Its variation may be due to changes in the properties of the material: in the type of distribution of stresses and structural defects, degree of dispersion, etc. Below we consider the characteristics of the kinetics of mechanochemical reactions which are typical for polydisperse systems. Examples of such reactions are those in polymers (distribution with respect to chain length) and comminution of solids (distribution with respect to particle size). The kinetics of reactions in polydisperse systems have been analysed in greater detail for the mechanical degradation of macromolecules[52].

The absorption of mechanical energy by macromolecules and at the same time the rate of the mechanochemical reaction depend on the length of the macromolecule—the degree of polymerisation. As a result of the dissociation of bonds, the degree of polymerisation falls and therefore, under steady-state conditions of mechanical treatment, the rate of bond dissociation will not be constant: its variation will be caused by changes in the molecular weight distribution of the polymeric substance during the reaction. Other conditions being equal, the kinetic equation for the degradation is determined by the form of the variation of the elementary rate constant with the length of the polymer chain. The formal kinetics of such reactions have been developed by Palov[52] and the subsequent treatment has been taken from his paper.

We shall denote the rate constant for the decomposition of molecules with a length equivalent to z units by $k(z)$. Then the following relation holds for the rate of increase of the number of molecules in the system:

$$\frac{dn}{d\tau} = \sum_1^\infty k(z) n_z, \tag{7}$$

where n is the total concentration of molecules and n_z the concentration of molecules with a length z. After dividing both parts of Eqn. (7) by $n = \sum_1^\infty n_z$, we obtain

$$\frac{d\ln n}{d\tau} = \frac{d\ln n/n_0}{d\tau} = \frac{\sum_1^\infty k(z) n_z}{\sum_1^\infty n_z} = [\overline{k(z)}], \tag{8}$$

where n_0 is the initial concentration of the species and $[\overline{k(z)}]$ is by definition the number average of $k(z)$. Bearing in mind that $n/n_0 = P_0/P$, where P_0 and P are the initial and actual number-average degrees of polymerisation, we finally obtain

$$\frac{d\ln(P_0/P)}{d\tau} = [\overline{k(z)}]. \tag{9}$$

This equation describes the rate of degradation as characterised by the left-hand side in terms of the average rate constant for the decomposition of the macromolecules. Since it is impossible to predict beforehand the type of variation of $k(z)$, in the general case Eqn. (9) cannot be given a concrete form. If it is assumed that the degradation rate constant is independent of the length of the macromolecule [$k(z) = k$], then

$$\frac{d\ln(P_0/P)}{d\tau} = k \text{ and } P = P_0\exp(-k\tau). \tag{10}$$

When the rate constant is directly proportional to the length of the polymeric molecule $k(z) = k_1 z$, the kinetic equation $d\ln(P_0/P)/d\tau = k_1 P$ assumes the following form after solution:

$$\frac{1}{P} - \frac{1}{P_0} = k_1\tau \tag{11}$$

which is characteristic of the so called random degradation.

Random degradation occurs on ultrasonic treatment of polymers in cavitation fields when chains are actually ruptured by active radicals formed when the cavities are flooded and not as a result of the direct action of shear stresses. The characteristic changes in the molecular weight distribution have been examined by Jellinek and White[53].

Using Eqn. (9), it is also possible to solve the converse problem, the determination of the form of the variation of the elementary rate constant with chain length from data on the decrease of the degree of polymerisation in the degradation process. We shall postulate that $k(z) = \delta k(P)$, where δ is a coefficient which depends on the variance in

the distribution of molecules with respect to length; then the variation of $d\ln(P_0/P)/d\tau$ with P is the same as the variation of $k(z)$ to within the coefficient δ. Figs. 7*a* and 7*b* show [52] the variation of $k(z)$ plotted by graphical differentiation for the ultrasonic degradation of polystyrene in solution. The kinetic curves analysed were taken from different studies [40,50] with markedly differing conditions (concentration, frequency, and ultrasonic power). Although the form of the $k(z)$ curves is different, they both show clearly the existence of the so called degradation limit—the minimum chain length on reaching which the degradation rate constant falls almost to zero. Thus under the specified conditions mechanical degradation is possible only for macromolecules with lengths above a specific limit.

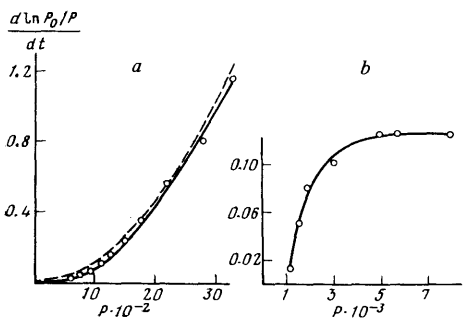

Figure 7. Variation of the rate constant with the degree of polymerisation in the ultrasonic treatment of polystyrene solutions: *a*) Schmid's data [54]; *b*) data of Berlin and El'tsefon [40].

The existence of the limit, associated with a sharp decrease of the rate of the mechanochemical process when the particle size diminishes, is the most characteristic feature of reactions in polydisperse systems. The limiting particle size enters into almost all the kinetic equations: the empirical Schmid equation [54], the Baramboim equation [1] corresponding to the degradation of macromolecules at "weak" bonds, the Schrader equation for the comminution of solids, and others. With increase in particle size, the rate constant rises sharply. Under these conditions, the quadratic relation $k(z) = k_2z^2$ is comparatively common. In the kinetics of the mechanical degradation of macromolecules, the Schmid equation [52] corresponds to the quadratic law. A relation of the type $k(z) = k_2z^2$ was observed also in the comminution of solids in surface-active media [55].

Rigorous analysis of kinetic data combined with the derivation of a relation for $k(z)$ is apparently possible only for mechanochemical processes in liquid media (degradation of polymers in solution, dispersion of solids in an aqueous medium, etc.) when the individual species are fairly well stabilised.

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The above very brief discussion of the formal kinetics of mechanochemical reactions shows that the rate of the process may be related to various parameters which depend on external conditions: to the inhomogeneity of the distribution of mechanical stresses throughout the bulk of the substance, the relaxation times of the stresses, and the characteristics for the absorption of mechanical energy by species of different size; finally, when the rate-limiting stage is the primary chemical step, the bond strength and vibration frequency enter into the kinetic equation.

Other factors with a marked influence on the rate of mechanochemical reactions undoubtedly exist. These include primarily the effect of mechanical stresses on the rate of diffusion of species in the condensed phase. This problem is not considered in the present review.

III. POSSIBLE MECHANISMS OF MECHANOCHEMICAL REACTIONS

Mechanochemical reactions differ from other chemical reactions initiated by physical methods in that they can develop with a comparatively low average level of elastic energy per unit volume of the substance. In photochemistry the energy quanta are comparable to the excitation energies for the electronic levels of the molecules. In radiation chemistry the energy of the particles acting upon the substance greatly exceeds the energies of the chemical bonds and one of the tasks in investigations of this kind is to follow the pathways in the dissipation of the excess energy. In the analysis of a mechanochemical process an attempt is made in the first place to deduce the mechanisms of the concentration of energy at individual bonds or in small local volumes in the substance.

Apparently there exist two direct mechanisms for the conversion of elastic into chemical energy which are specific to mechanochemistry: the first of these is associated with the deformation of the electron clouds of the reacting species (a change in the interatomic distances, valence angles, etc.) and the second with the vibrational excitation of the bonds during the dissipation of elastic energy as heat. The first mechanism may be referred to as the equilibrium mechanism, since the equilibrium Maxwell–Boltzmann distribution of energy among the degrees of freedom persists in the system, while the second is a non-equilibrium mechanism.

1. The Equilibrium Process

When a chemical bond is extended, its energy diminishes. At equilibrium, the deformation energy is

$$U_{\text{def}} = \int_{r_0}^{r} f_U dr \quad \text{or} \quad U_{\text{def}} = \int_{V_0^*}^{V^*} \sigma_U dV^*, \tag{12}$$

where f_U and σ_U are the force and the stress acting on the bond, r_0 and r are the length of the initial and the deformed bond, and V_0^* and V^* are the corresponding activation volumes; $V^* = rs^*$ and s^* is the effective cross-section of the molecule (bond) is relation to the applied stress.

In calculations of the deformation energy and the activation energy for bond dissociation when a force f_U operates, one usually employs the Morse potential function. The variation of the activation energy for decomposition with the force f_U is [56]

$$\frac{U}{U_0} = \sqrt{1-\frac{f_U}{F_0}} - \frac{f_U}{2F_0}\ln\frac{1+\sqrt{1-\frac{f_U}{F_0}}}{1-\sqrt{1-\frac{f_U}{F_0}}}, \tag{13}$$

where F_0 is the ultimate strength of the bond. A plot of the function $L(f_U)$ is presented in Fig. 8 (curve *1*). Under real conditions, a specific group of bonds are deformed; the characteristic features of the energy relations of the process in this case have been analysed [57]. The functions $U(f_U)$ corresponding to the extension of sections of the macromolecule with lengths equivalent to 10, 20, 50, and 100 bonds are compared in Fig. 8 (curves *2–5*) [57].

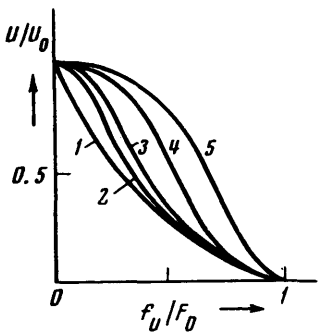

Figure 8. Plot of the function $U(f_U)$; number of bonds in deformed section of chain: 1) ∞; 2) 100; 3) 50; 4) 20; 5) 10.

Eqn. (13) in fact describes the simplest case of the conversion of mechanical into chemical energy and is used to account for the dissociation of mechanically strained bonds. Eqn. (13) is approximate: in complex molecules account must be taken of the deformation of valence angles, angles of internal rotation, and the interaction between atoms not linked by valence bonds [58].

The activation energy for thermal decomposition reactions in the Arrhenius equation is the same as the bond energy U_0:

$$k = k_0 \exp\left(-\frac{U_0}{RT}\right), \qquad (14)$$

where k is the decomposition rate constant (s^{-1}) and k_0 the pre-exponential factor, close to 10^{12}–10^{13} s^{-1} in order of magnitude. When the bonds are mechanically strained, U_0 may be replaced by the expression for the strength of an elastically deformed bond [$U(f_U)$, see Fig. 8]:

$$k_M = k_{0,M} \exp\left(-\frac{U(f_U)}{RT}\right). \qquad (15)$$

An analogous approach based on estimates of the decrease of the energy barrier to purely thermal transitions under the influence of "weak" factors is frequently employed in the analysis of the kinetics or thermodynamics of various processes (diffusion processes, migration of dislocations, effect of the medium on the equilibrium position, etc.). Thus in an equilibrium process the role of mechanical stresses reduces to a decrease of the energy barrier in the thermal reaction. A direct purely mechanical dissociation of bonds without the involvement of thermal fluctuations is possible only when stresses exceeding the bond strength F_0 are applied during a time less than the vibration period (10^{-12}–10^{-13} s). This implies that, for a bond length of the order of 10^{-10} m the rate of propagation of stresses

$$w \simeq \frac{10^{-10}}{10^{-12}-10^{-13}} \simeq 10^{2}-10^{3} \text{ m s}^{-1},$$

must be comparable to the velocity of sound. Probably this limiting case of a purely mechanical rupture occurs under the conditions of a severe stress, for example under the action of shock waves.

The most striking example of a mechanochemical process with an equilibrium mechanism is the degradation of molecules on deformation (monoaxial extension) of polymeric films or fibres. Here all the consecutive stages of the process have been investigated experimentally.

The existence of strained bonds in the main valence chain in polymeric materials subjected to mechanical deformation has been recently demonstrated by infrared spectroscopy [59–61]. Fig. 9*a* shows [61] the variation of the form of the 975 cm^{-1} band corresponding to the skeletal vibrations in oriented polypropylene on monoaxial extension of the specimen. Under load, the position of the maximum shifts insignificantly but the line contour becomes greatly extended towards longer wavelengths, which reflects the existence of a continuous distribution of bonds overstrained to different extents. The frequency $\nu \simeq 940$–950 cm^{-1} corresponds to the bonds deformed to the maximum extent. The distribution function of external stresses with respect to the chemical bonds of the specimen, obtained by analysing the form of the line contour for $\sigma = 84$ kgf mm^{-2}, is plotted in Fig. 9*b*. [61] The distribution is extremely inhomogeneous and extends far into the region of high stresses. According to the first estimates, the maximum stresses reach $\sigma_{max} \simeq 1000$ kgf mm^{-2}; since the decomposition rate constant increases exponentially with increase of the true stress [Eqn. (15)], the degradation process should be virtually confined to bonds subjected to maximum stress.

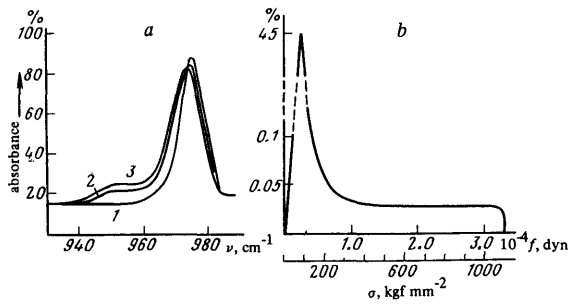

Figure 9. *a*) Variation of the absorption band contour at 975 cm^{-1} in oriented polypropylene under load [applied load (σ, kgf mm^{-2}): 1) 0; 2) 65; 3) 80]; *b*) distribution of stresses with respect to bonds.

The decomposition of the strained parts of the chains is confirmed by the formation of free radicals as a result of the dissociation of chemical bonds. Free radicals have been detected in monoaxial extension processes in various polymers directly in the resonator of an ESR spectrometer and also in cold-drawn specimens [62–71].

Under the conditions where σ = const., the rate of formation of radicals, which is proportional to the rate of dissociation of overstrained bonds, depends on the stress according to the law [64]

$$\frac{d[R^{\cdot}]}{d\tau} = B\exp(\beta\sigma),$$

where B and β are constants.

Over a wide range of variation of external parameters (σ and T), $d[R^{\cdot}]/d\tau$ agrees well with the rate of decomposition of the specimens. The logarithms of the rates of formation of radicals (corresponding to the steady-state sections of the kinetic curves) are plotted in Fig. 10 against the lifetimes of the specimens [64]; all the points are located on a single straight line with a slope of unity. The kinetics of the accumulation of radicals and the formation of submicrocracks—the primary breaks in the continuity of the material—likewise proved to be similar in polymers [71].

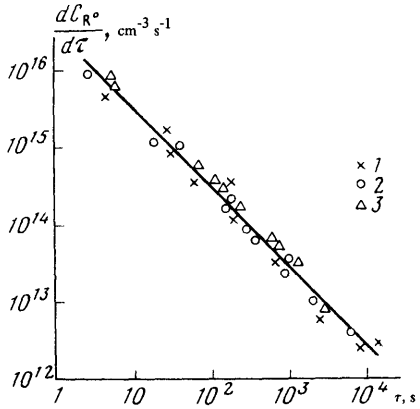

Figure 10. Relation between the rate of formation of radicals and their lifetime in oriented Kapron: 1) −50°C; 2) +18°C; 3) +50°C.

All these data and also the results of many other investigations (see, for example, Pozdnyakov and Regel' [72]) convincingly confirm the reality of the equilibrium mechanism of dissociation of deformed bonds and also the thermal-fluctuation concept of the strength of solids based on this mechanism [8].

The equilibrium processes include the corrosion of metals under stress. A theory has been developed which takes into account the effect of the perturbations of the electronic levels in metals, associated with the generation of dislocations, on the standard electrode potential [73].

2. The Non-equilibrium Process

Mechanochemical reactions can develop not only under stress but also during the removal of stresses or during their redistribution in the substance when elastic energy is transformed into thermal energy [9,46]. In a material subjected to elastic stress, the bonds of the framework of the substance which withstand the mechanical stress are mainly deformed and when the stresses are removed, thermal (vibrational) energy is liberated at these bonds. For example, at the instant of contraction of the macromolecule one may expect vibrational excitation of the bonds in the main chain. Subsequently the vibrational excitation energy is redistributed among all the degrees of freedom of the system. In other words, since the entire flux of elastic energy dissipated as heat passes through the bonds of the main chain, it follows that, for a certain definite period τ^*, these bonds are in a vibrationally excited state.

The conversion of the elastic energy of the deformed bonds (U_{def}) into thermal energy (Q_{therm}) can be represented schematically as follows:

$$U_{def} \rightarrow \Delta U_{vibr} \rightarrow Q_{therm}$$

where ΔU_{vibr} is the vibrational excitational energy of the deformed bonds.

Under steady-state conditions the concentration of the vibrationally excited bonds $[A^*]$ is defined by the relation

$$[A^*] \simeq \tau^* \frac{dU_{def}}{d\tau} . \qquad (16)$$

The lifetime of the vibrationally excited states in solids is short and hardly exceeds 10^{-10} s (i.e. corresponds to 10^2–10^3 vibration periods). During the time τ^*, the excitation energy can either pass to other degrees of freedom of the system or can give rise to a mechanochemical reaction; if τ_{chem} is the characteristic reaction time, the ratio τ^*/τ_{chem} defines the probability of reaction during the lifetime of the vibrationally excited state. When $\tau^*/\tau_{chem} \geq 1$, excitation always leads to reaction.

In order to estimate qualitatively τ_{chem}, one may postulate that, during the dissipation of elastic energy, excitation extends over a region sufficiently large to employ the concept of the vibrational temperature T^*. To a very rough approximation, $RT^* \simeq \Delta U^*_{vibr}$; then, for example for the bond dissociation energy [46] (with $\Delta U_{vibr} \gg RT$),

$$\tau_{chem} \simeq \tau_0 \exp\left(\frac{U_0}{\Delta U_{vibr}}\right) \qquad (17)$$

or in the general case

$$\tau_{chem} \simeq \tau_0 \exp\left\{\frac{U(f_U)}{\Delta U_{vibr}}\right\} .$$

For the inequality $\tau^*/\tau_{chem} \geq 1$ to hold, it is necessary that

$$\Delta U^*_{vibr} \geqslant \frac{U(f_U)}{\ln\frac{\tau^*}{\tau_0}} , \qquad (18)$$

i.e. the dissipation of energy greater than ΔU^*_{vibr} will always lead to bond dissociation. The critical energy ΔU^*_{vibr}, necessary for the dissociation of the bond during the period τ^*, is appreciably less than the bond energy U_0; when $\tau^* = 10^2\tau_0$, $\Delta U^*_{vibr} \simeq 0.2U$.

The rate of the mechanochemical reaction is proportional to the concentration of the vibrationally excited bonds $[A^*]$ and consequently [16] the rate of dissipation of elastic energy as heat is

$$\frac{dC}{d\tau} \simeq \tau^* \frac{dU_{def}}{d\tau} , \qquad (19)$$

Thus the principal feature of the non-equilibrium mechanism is that the rate of the mechanochemical reaction is determined by the rate of relaxation of the elastic energy in the system.

The non-equilibrium mechanism of mechanochemical reactions can be confirmed either by direct spectroscopic measurements or on the basis of a series of indirect chemical characteristics. There are so far no spectroscopic data in the literature, but the first chemical measurements have already been made [46]. In polymers the dissociations of the vibrationally excited sections of the chains should lead to the formation of hot macroradicals capable of further chemical reactions at low temperatures where the usual thermal reactions are retarded. The most probable reaction of hot radicals is decomposition with formation of low-molecular-weight compounds. Fig. 11 presents the results of measurements of the amount of low-molecular-weight products formed on mechanical breakdown of polyisobutylene and polyformaldehyde powders in a mill at −78°C. [46] At the same time measurements were made of the concentration of radicals by ESR. In all the experiments the amount of low-molecular-weight decomposition products (mainly monomeric compounds—isobutene and formaldehyde) exceeds by severalfold the concentration of the radicals formed, i.e. the excess vibrational energy is sufficient for the ejection of several monomeric units.

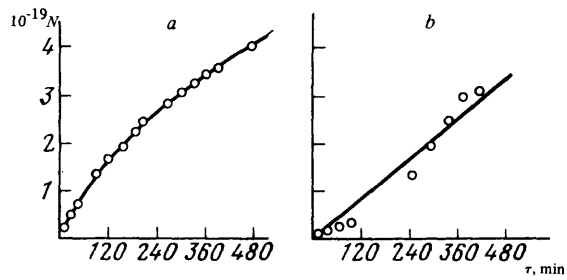

Figure 11. Formation of low-molecular-weight products in the mechanochemical disintegration of polyisobutylene (*a*) and polyformaldehyde (*b*) powders at −78°C.

The data in Fig. 11 and also the measurements of the amount and composition of volatile products evolved during the extension and after the rupture of polymeric films [72, 74,75] at higher temperatures confirm the occurrence of chemical decomposition reactions during the dissipation of elastic energy.

The possibility of the dissipation of energy after the dissociation of macromolecules [76] or after "ejection" of energy on breakdown of a solid subjected to an elastic stress [77] are usually discussed in an examination of the correspnding processes. As already pointed out, elastic deformation and non-equilibrium excitation are consecutive stages of the same process. The essential feature of the non-equilibrium mechanism [46] consists in the fact that the dissipation of an amount of the elastic energy stored by the system less than is required for its breakdown leads to the generation of non-equilibrium excited states, resulting in chemical reactions including bond dissociations and degradation of the macromolecules.

The generation of non-equilibrium vibrationally excited states was recently postulated in connection with the explanation of the kinetics of the photochemical degradation of mechanically strained macromolecules [78].

3. Local Regions of the Absorption of Elastic Energy

The direct pathways for the conversion of elastic into chemical energy discussed above do not cover all the hypotheses which have been put forward concerning the nature of mechanochemical reactions. In ultrasonic chemistry [19,79,80,81], in tribochemistry [10,82], in the theory of impact detonation of explosives [30,31], and in the chemistry of shock-waves [28], models explaining the occurrence of mechanochemical reactions as a result of the generation of local regions where elastic energy is concentrated and absorbed in the bulk or in the surface layer of the substance are widely used. The duration of the existence of such local regions is short and in various hypotheses is estimated as 10^{-3}–10^{-6} s and less, their radius being 10^{-3}–10^{-7} cm. The high pressures and the intense heating in the local regions initiate chemical reactions.

Among the existing theories of the conversion of elastic energy in small volumes within the substance, only the theories of the propagation of shock waves and cavitation have been comparatively thoroughly developed.

In ultrasonic fields and in turbulent flow, the local absorption of elastic energy is associated with the phenomenon of cavitation. Cavitation—local, point disruption of the liquid with the appearance of cavities filled by the dissolved gas and the saturated vapour of the liquid—constitutes an unusually effective mechanism of the absorption of the energy of elastic vibrations in liquids. Chemical reactions begin when the cavities collapse during the contraction phase of the sonic wave. The high pressures (10^4 atm) and temperatures (thousands of degrees) developed in the stage of the adiabatic compression of the bubble [19] lead to the excitation and dissociation of the molecules filling it; after collapse, the active species [83] (in aqueous solutions H atoms, OH radicals, hydrated electrons [84,85], etc.) pass into solution where they can initiate various oxidation reactions, polymerisation, and many other processes. Adiabatic compression of gas bubbles is among the processes involved in the initiation of the detonation of explosives by impact [86].

The brief existence of local regions with high pressures and temperatures (the shock wave front, the "hot spots" in the friction of solids, the magma–plasma model, etc.) has been confirmed by various model experiments. However, the specific features of mechanochemical reactions, the direction of the process, its rate, etc. cannot always be accounted for by purely thermal effects or the simultaneous action of heat and pressure.

The chemical and physicochemical reactions in shock waves are unusually rapid ($\tau \ll 10^{-6}$ s) [88], much more rapid than would be expected on the basis of the existing hypotheses concerning the growth of the nuclei of a new phase or the mechanisms of diffusion in a condensed phase [28]. For such ultrafast processes, the term "diffusion-free" reactions has been proposed. It has been suggested [87] that, at the pressures developed in the shock-wave front, the substance passes into the state of a single activated complex, close to the metallic state characteristic of high degrees of compression. On releasing the pressure after the passage of the shock wave, the form of matter stable when the degree of expansion corresponds to the instant of decomposition of the single activated complex becomes stabilised (this is because electronic transitions are much faster than the rearrangement of atoms). This hypothesis has been put forward to account for the polymorphic transformations of the graphite–diamond type in powerful shock waves. Outwardly similar hypotheses concerning the rapid "quenching" of different

forms of a substance, corresponding to the instant when "hot spots" exist, have been used in the mechanochemistry of solids.

The specific features of mechanochemical processes are also associated with plastic deformation and the nature of the strained state of the substance. Pressure and temperature can supply sufficient energy for the reaction to occur (they can create a "thermodynamic background" [28]), but it is also necessary that mechanical stresses should act in the same direction as the reaction. Thus, in the mechanical degradation of macromolecules, sheer or tensile stresses not only dissociate the bonds in the main chain but they also liberate from the "cages" the radicals formed and prevent their recombination. In polymerisation it is not sufficient to set up a pressure at which the density of the monomer becomes comparable to that of the polymer; it is also necessary to consider the possibility of chain propagation, which is achieved by plastic deformation of the material with simultaneous application of pressure and sheer deformation [26,27].

IV. PRIMARY ACTIVE CENTRES IN MECHANOCHEMICAL REACTIONS

In the analysis of the elementary mechanisms of various mechanochemical reactions, it is important to know the nature of the primary active species or surface centres formed as a result of the transformations of elastic energy. Information about the nature of the primary centres has been obtained mainly in studies on the mechanical degradation of macromolecules, certain organic reactions, chemical reactions in ultrasonic fields, and, to a lesser extent, in processes involving the disruption of solids.

According to the most general considerations, in the ideal case of the dissociation in vacuo of chemical bonds of different types (ranging from homopolar to purely ionic), the formation of electrically neutral decomposition products is more favourable on energy grounds. In principle, two cases are possible:

$$\sim A-B\sim \begin{cases} \longrightarrow \sim A^{\cdot} + {}^{\cdot}B\sim \text{ (I)} & U_{A-B} \\ \longrightarrow \sim A^{+} + {}^{-}B\sim \text{ (II)} & U_{A-B}+(I_A-A_B). \end{cases}$$

In the first case the energy expenditure is equal to the strength of the A–B bond, while in the second case it is necessary to supply additional energy equal to the difference between the ionisation potential of the fragment $\sim A(I_A)$ and the electron affinity of the species $B\sim(A_B)$. In the dissociation of bonds in compounds of the alkane series this difference approaches

$$I_{C_2H_7} - A_{C_2H_7} = 8.7-1.0 = 7.7 \text{ eV} \simeq 170 \text{ kcal mole}^{-1}.$$

In the majority of organic reactions, the difference $I - A$ in the dissociation of bonds is somewhat less, but nevertheless remains considerable; thus the electron affinities of certain radicals may reach 1.5–2.0 eV, but the ionisation potentials of molecules or their fragments are rarely less than 6 eV; therefore the difference $I - A$ can hardly be less than 4–5 eV.

In exactly the same way, when the typically ionic compound NaCl decomposes in a vacuum,

$$I_{Na} - A_{Cl} = 5.14-3.81 = 1.33 \text{ eV} \simeq 30 \text{ kcal mole}^{-1},$$

i.e. even in this limiting case of an ionic bond the formation of electrically neutral Na and Cl atoms remains more favourable than the formation of Na^+ and Cl^- ions. Recently it was established that, in the mechanical disruption of NaCl crystals, sodium (it was referred to as the amalgam) and gaseous chlorine are evolved in considerable amounts[89].

In polar media, where there is a possibility of an energy gain owing to the solvation or polarisation of the species formed, the situation may alter significantly. One may expect that in the majority of organic substances the main pathway for bond dissociation in mechanical disruption (and also in thermal degradation) is radical or molecular but not ionic. All the experimental data accumulated hitherto are consistent with these general considerations: in the mechanical disruption of carbon chain and heterochain organic polymers, free radicals are formed. Initially they were detected by the acceptor method[1–5], but in the last decade vigorous investigations of the free-radical products of the mechanical degradation of polymers by ESR began [90,91].

The dissociation of linear macromolecules with formation of radicals has been observed in solutions under the influence of sheer and ultrasonic gradients and in polymeric substances in the rubber-elastic, vitreous, and crystalline states.

Table 3. The structure of the primary free radicals formed in the mechanical rupture of polymer chains.

Substance	Structure of radicals	References
Polyethylene	$\sim CH_2\dot{C}H_2 + \dot{C}H_2CH_2\sim$	92,93
Polytetrafluoroethylene	$\sim CF_2\dot{C}F_2 + \dot{C}F_2CF_2\sim$	94
Polystyrene	$\sim CH(C_6H_5)\dot{C}H_2 + \dot{C}H(C_6H_5)CH_2\sim$	95
Polyamides	$\sim CH_2\dot{C}H_2 + \dot{C}H_2(NHCO)\sim$	93
Poly(ethylene oxide), poly(ethylene sulphide) (X = O or S)	$\sim X\dot{C}H_2 + \dot{C}H_2X\sim$	96,97

The structure of the primary radicals has been elucidated by ESR, i.e. the sites of the preferential mechanical rupture of polymer chains have been established (Table 3), quantitative measurements of the rates of bond dissociation under various conditions of disruption of polymeric materials have been begun (monoaxial extension [62–64,69], comminution [46], etc.), and the direction and kinetics of secondary free-radical reactions are being investigated, i.e. the further fate of radicals is being traced [92,98–103].

Active species capable of initiating various chemical reactions, including chain processes have been detected also when low-molecular-weight substances are subjected to mechanical action.

In ultrasonic fields (cavitation conditions) chemical reactions are initiated by the free-radical decomposition products of water [83]. The decomposition of H_2O can occur either as a result of a sharp adiabatic compression of the cavity [19,79] or under the influence of microdischarges (electrical breakdown of the cavity) in the stage of its formation [80] or its collapse [81]. None of these mechanisms can so far be rejected. Hydrated electrons were recently detected [84] in water decomposition products:

$$H_2O \xrightarrow{u.s.} OH^{\cdot}, H^{\cdot}, H_2O_2, e^-_{aq.} \text{ etc.}$$

The probabilities of various elementary processes leading to the formation of excited species, radicals, and ions in the cavity have been compared in a review [85]. The chemical effect of ultrasonic cavitation resembles in broadest outline the indirect effect of radiation on aqueous solutions.

One of the most sensitive methods for demonstrating the existence of active species in various systems is the

initiation of chemical chain reactions. Chain polymerisation was observed in ultrasonic cavitation fields [104,105] (in the absence of traces of water there is no polymerisation [106]), in shock waves [107-109], under the influence of high pressures with shear [26,27,110], and finally in the mechanical dispersion of solids [111-114]. In the last two systems the reaction mechanism was established by measuring the copolymerisation rate constants: when high pressures with shear operate, the reaction is propagated by free radicals [110] and in the comminution of the monomer together with various solids, polymerisation is caused by the effect of charged species [114,115] and possibly of emission electrons [115].

The problem of the analysis of the nature of the primary centres is much more complex in the mechanochemistry of solids where it is necessary to take into account not only the dissociation of various bonds but also the behaviour of the entire crystal and its surface. The primary active states in solids are investigated by adsorption, low-temperature electron emission, luminescence, ESR methods, etc. The results of studies on the nature of paramagnetic centres detected by ESR in solids of different types are compiled in Table 4. Analysis and interpretation of the ESR spectra in polycrystalline solids constitutes a fairly complex problem and as a rule the nature of the centres has been established indirectly by the analysis of their physical and chemical properties.

As already mentioned, in complex organic reactions free radicals are formed. When the two-dimensional networks of graphite are broken, free radical centres are formed on the basal planes, their concentration reaching 10^{14} cm^{-2}. There is at present no unanimous view concerning the nature of the paramagnetic centres in silicon. Judging from chemical characteristics, a considerable proportion of the centres detected in SiO_2 are of a free-radical type, but this has not been demonstrated convincingly.

Table 4. The nature of the paramagnetic centres detected in the mechanical disintegration of certain materials.

Polymer	Free radicals	Charged states	References
Cellulose	+	—	116, 117
DNA	+	—	118
Horns and hooves	+	—	119
Graphite	+	—	120, 121
Silicon	?	—	122—130
Silicon carbide	+	—	131
Quartz	?	—	90, 125, 132—138
Germanium dioxide	—	+	139
Barium sulphate	—	+	90, 139

Charged states (electrons in shallow traps) stable only at a low temperature have been detected in both GeO_2 and $BaSO_4$. One may suppose that the formation of charged centres is part of the range of mechano-emission phenomena accompanying the mechanical disruption of solids and reflected in static electrification [140], luminescence [10], electron emission [141,142], etc. There is so far no general theory of emission phenomena. In the electrical theory of adhesion [143,144] the emission of high-energy electrons is explained by the formation of an electrical double layer at the surfaces in contact. When the adhesion contact is broken, a powerful electric field abstracts electrons from the surface and disperses them. Electrical excitation of matter can occur as a result of the interaction of elastic waves with current carriers (the electroacoustic effect) [145-147]; the polarisation of substances in shock waves is apparently associated with this mechanism [148,149]. The emission and luminesence on friction and on impact by solids has also been explained within the framework of the magma–plasma model [10].

Electro-emission phenomena are of great importance for mechanochemistry, since an electrical discharge between solid surfaces or a planar surface discharge [150] can lead to the formation of active species, including electrons, which initiate various chemical reactions [115].

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Mechanochemical phenomena occur widely in nature and are of considerable importance for many branches of science and engineering; these are the problems of the strength of solids and of the physicochemical mechanics of materials, certain branches of colloidal chemistry, the physics and physical chemistry of polymers, geochemistry, biophysics, the technology of inorganic substances, and chemical kinetics, the theories of the reactivity of molecules and molecular acoustics, and problems of friction and wear, heterogeneous catalysis and adsorption, detonation and propagation of shock waves, metal corrosion, etc. Mechanochemical reactions are of a wide variety of types and at first sight it is difficult to compare processes involving the absorption of sound in gases with chemical changes in the friction of solids or reactions in shock waves with corrosion of a mechanically strained metal. However, the chemical reactions are throughout induced by the absorption of elastic energy and these widely differing processes have common features reflected in the nature of the primary steps and their kinetics. In the present review particular attention has been devoted to these problems in the analysis and classification of published data. Many no less important aspects of mechanochemical reactions have not been mentioned or only touched upon: the process energetics and thermodynamics, the relation between mechanochemistry on the one hand and physicochemical mechanics and processes involving the disruption of materials on the other [77], mechano-emission phenomena, processes in which a substance is subjected to the simultaneous action of various types of energy [78,151] (for example elastic and emission energies), the characteristics of reactions in inorganic substances [152], the generation of luminescence and the occurrence of gas-discharge processes [153], etc.

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The Chemistry of Acyl Radicals in Solution

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The available methods for the generation of acyl radicals and their reactions in solutions are reviewed. The effect of stabilising and polar factors on the reactivity of acyl radicals and the mode of their addition to unsaturated molecules are discussed. The characteristics of the reactions involving acyl radicals, initiated by various methods (by peroxides, ultraviolet light, γ-irradiation, etc.) have been examined. Much attention has been devoted to the role of acyl radicals in chain processes constituting the basis of new methods for the synthesis of carbonyl compounds.
The bibliography includes 266 references.

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I. INTRODUCTION

Acyl radicals are some of the simplest carbonium radicals. In 1949 Kharasch et al.[1] proposed a method for their preparation from aldehydes with the aid of peroxides and ultraviolet light. In the next 20 years numerous studies were made on the reactivity of acyl radicals and their role in liquid-phase homolytic processes was investigated. Owing to the ease of formation of acyl radicals in solution, they are finding increasing application in organic synthesis.

At the present time there are six main methods for the generation of acyl radicals in solution:

1. Homolytic removal of hydrogen from aldehydes:

$$R-C\begin{matrix}H\\ \diagup\\ \diagdown\\ O\end{matrix} + A\cdot \rightarrow R-\dot{C}=O+AH\,.$$

2. Homolytic removal of a halogen from acid halides:

$$R-C\begin{matrix}X\\ \diagup\\ \diagdown\\ O\end{matrix} + A\cdot \rightarrow R-\dot{C}=O+AX\,.$$

3. Thermal, photolytic, or radiolytic dissociation of ketones and carboxylic acid derivatives:

$$R-C\begin{matrix}Y\\ \diagup\\ \diagdown\\ O\end{matrix} \rightarrow R-\dot{C}=O+Y$$

(Y = alkyl or a functional group).

4. One-electron oxidation of aldehydes:

$$R-C\begin{matrix}H\\ \diagup\\ \diagdown\\ O\end{matrix} + M^n \rightarrow R-\dot{C}=O+M^{n-1}+H^+ \quad (M\text{—metal})\,.$$

5. Addition of carbon monoxide to alkyl radicals:

$$R^\cdot + CO \rightarrow R-\dot{C}=O\quad .$$

6. Decomposition of more complex radicals, for example:

$$R-\underset{\displaystyle R'}{\overset{\displaystyle \dot{O}}{\underset{|}{C}}}-\overset{\displaystyle O}{\overset{\|}{C}}-R'' \rightarrow R''\dot{C}=O + R-\overset{\displaystyle O}{\overset{\|}{C}}-R'\,.$$

The radicals R–Ċ=O readily add to multiple carbon–carbon bonds and also to the bonds >C=O, >C=N–, –N=N–, etc. At elevated temperatures they lose carbon monoxide and are converted into alkyl radicals. Many photochemical rearrangements and decompositions of aldehydes, ketones, and carboxylic acid derivatives involve acyl radicals.

The radicals R–Ċ=O generated in solution are usually identified on the basis of the products of their further reactions. Owing to the short lifetime of acyl radicals in the liquid phase, their ESR spectra[2–5] can be obtained only at low temperatures (in the frozen state).

The present review deals with studies on the methods of generation and reactions of acyl radicals published up to 1970.

II. METHODS OF GENERATION OF ACYL RADICALS

1. FORMATION OF ACYL RADICALS FROM ALDEHYDES

In the generation of acyl radicals from aldehydes, compounds which readily undergo thermal dissociation (organic peroxides, azo-compounds, etc.), oxygen, and variable-valence metal salts are most often employed. Acyl radicals are also obtained by allowing ultraviolet light or γ-rays to act directly on aldehydes.

The relative reactivities of various aldehydes in reactions involving the removal of a hydrogen atom by t-butoxy-radicals have been investigated[6–8]. The t-butoxy radicals were obtained from t-butyl hypochlorite. The reaction has a chain mechanism, the chain being probably initiated as a result of the trimolecular reaction

$$2\,(CH_3)_3COCl + RCHO \rightarrow 2\,(CH_3)_3C-O\cdot + HCl + RCOCl\,.$$

The removal of a hydrogen atom by the $(CH_3)_3CO\cdot$ radical from CH_3CHO and from C_6H_5CHO is faster by a factor of 4.3 and 3.4 respectively than from cyclohexane[6]. *m* and *p*-Nitrobenzaldehydes do not react with $(CH_3)_3COCl$[7] owing to the electrophilic properties of t-butoxy-radicals. In this case the polar factor promotes an increase of activation energy, which hinders the removal of a hydrogen atom[6]. Probably this is why the removal of hydrogen from n-butyraldehyde by perbenzoate radicals is much easier than from benzaldehyde[9].

The relative reactivities of substituted benzaldehydes in the reaction with sulphuryl chloride initiated by benzoyl peroxide have been investigated by the method of competing reactions. Aroyl radicals are generated as a result of an attack on the aldehyde by the $\cdot SO_2Cl$ radical[10-12]. The values obtained are correlated in terms of the Hammett equation ($\rho = -0.48$). The effect of substituents is determined by the role of polar factors in the transition state[12]:

$$RC\overset{O}{\underset{H}{\diagup}} + \cdot SO_2Cl \rightarrow RC\overset{\delta+}{\underset{O}{\cdots}}H\cdots\overset{\delta-}{SO_2Cl} \rightarrow R-\dot{C}=O + SO_2 + HCl\,.$$

The relative reactivities of substituted benzaldehydes in the reaction with $\cdot CCl_3$ radicals were determined by Lee[13]. In this case $\rho = -0.74$. When C_6H_5CHO is replaced by C_6H_5CDO, the kinetic isotope effect is 2.4 at 80°C. $BrCCl_3$ was used as a source of $\cdot CCl_3$ radicals. The reactivities of C_6H_5CHO and other hydrogen donors with respect to the trichloromethyl ($\cdot CCl_3$)[14] and phenyl ($\cdot C_6H_5$)[15] radicals have been compared[14,15]. Table 1 lists the reactivities of C–H bonds in reactions involving the removal of hydrogen by certain radicals.

Table 1. Relative reactivities of various C–H bonds in reactions involving the abstraction of a hydrogen atom.

Radical	Compound				References
	$C_6H_5CH_3$	C_6H_5CHO	CH_3CHO	cyclohexane	
$(CH_3)_3C-O\cdot$	1	12.8	16.1	0.16	6
$\cdot SO_2Cl$	1	9.7	—	2.9	11
$\cdot CCl_3$	1	58	—	—	14

$\alpha\alpha'$-Azobisisobutyrate, a widely used initiator of many homolytic processes, has proved relatively ineffective for the generation of acyl radicals from aliphatic aldehyde[16]: only 15–20% of the total amount of $\cdot C(CH_3)_2-COO-CH_3$ radicals formed in the decomposition of the azo-compound removed hydrogen from the aldehyde, while the remainder recombined or added to the azo-group of the initiator.

When acrolein is attacked by t-butoxy-radicals, the reaction involving the removal of hydrogen from the aldehyde group predominates ($K_{rem}/K_{add} \geqslant 18$):[8]

$$(CH_3)_3COCl \xrightarrow{h\nu} (CH_3)_3C-O\cdot + Cl\cdot$$

$$(CH_3)_3C-O\cdot + CH_2=CHCHO \begin{cases} \xrightarrow{K_{rem}} CH_2=CH-\dot{C}=O + (CH_3)_3COH \\ \xrightarrow{K_{add}} (CH_3)_3COCH_2-\dot{C}H-CHO\,. \end{cases}$$

Acetyl radicals are generated in the catalytic chain oxidation of acetaldehyde by oxygen (catalysed by a cobalt salt)[17-19]. At an advanced stage of the reaction, the following elementary steps play a decisive role in chain initiation[19]:

$$CH_3CHO + Co^{III} \rightarrow CH_3-\dot{C}=O + Co^{II} + H^+\,,$$

$$CH_3\overset{O}{\overset{\|}{C}}-OO-\overset{OH}{\overset{|}{C}}HCH_3 + Co^{II} \rightarrow CH_3COO^- + Co^{III} + \cdot O-\overset{OH}{\overset{|}{C}}HCH_3\,.$$

Subsequently the $CH_3CH(OH)O\cdot$ radical removes hydrogen from the aldehyde, as a result of which $CH_3-\dot{C}=O$ is formed.

From a study of the kinetics of the oxidation of aromatic aldehydes by hydrated cobalt ions in aqueous acetonitrile, a mechanism was proposed for this reaction with intermediate formation of aroyl radicals[20]:

$$ArCHO + Co^{III} \rightarrow Ar-\dot{C}=O + Co^{II} + H^+\,.$$

A kinetic isotope effect of 2.3 at 10°C was observed in the oxidation of ArCDO. Consequently the rate-limiting stage of the process is the dissociation of the C–H(D) bond in the aldehyde group[20].

The $C_6H_5-\dot{C}=O$ radicals were obtained by the oxidation of C_6H_5CHO with cerium(IV) perchlorate in 85% acetic acid[21]. Acrylonitrile was used as the $C_6H_5-\dot{C}=O$ acceptor. Each molecule of polyacrylonitrile formed contained one benzoyl group.

Free radicals, most probably $C_6H_5-\dot{C}=O$, are generated in the oxidation of benzaldehyde by chromic acid[22] and chromyl acetate[23]. In the first case the radicals arise only after the appearance in the solution of chromium(IV), which is evidently responsible for their formation.

In contrast to aromatic aldehydes, aliphatic aldehydes are oxidised by transition metal ions in an aqueous medium in the hydrated[24,25] or enolic[26] forms. One may expect that alkoxy-radicals are generated in such cases. Recently a method has been proposed for the preparation of acyl radicals by the reaction of aliphatic aldehydes with manganese triacetate in the absence of a solvent of in glacial acetic acid[27]. The authors believe that this reaction proceeds via a stage involving the intermediate formation of a radical-cation[28]:

$$RCHO + Mn(OAc)_3 \rightarrow R-\overset{+}{\underset{H}{\overset{O}{\diagup}}}C\,[Mn(OAc)_3]^- \rightarrow R-\dot{C}=O + AcOH + Mn(OAc)_2\,.$$

When aldehydes are irradiated with ultraviolet light, acyl radicals are generated as a result of the secondary reactions of the excited molecules. The primary processes occurring in the photolysis of aldehydes have been fairly thoroughly investigated[29]. For the majority of aldehydes, the lowest excited state corresponds to an $n-\pi^*$ transition (i.e. the transition of one of the non-bonding $2p$ electrons of the oxygen atom to an antibonding π^* orbital of the carbonyl group). Since in the $n-\pi^*$ excited state aldehydes, like ketones, exhibit the properties of free radicals with an unpaired electron at the oxygen atom[30], they can remove hydrogen from other aldehyde molecules with formation of acyl free radicals:

$$RCHO \xrightarrow{h\nu} RCHO^*\,,$$

$$RCHO^* + RCHO \rightarrow R-\dot{C}H-OH + R-\dot{C}=O\,.$$

Although the decomposition of excited aldehyde molecules into $R-\dot{C}=O$ and a hydrogen atom has been observed under the condition of flash photolysis, nevertheless it does not play a significant role in photolytic reactions[29].

It is noteworthy that the use of ultraviolet light for the generation of $R-\dot{C}=O$ radicals from aldehydes frequently involves undesirable side processes, for example the cleavage of the aldehyde molecule with formation of an olefin (a Norrish type II cleavage)[29] or the polymerisation of the aldehyde to a cyclic trimer[31,32].

γ-Irradiation has been used to generate acyl radicals in free-radical reactions involving the addition of aldehydes to alk-1-enes (Section III). The study of γ-radiolysis of propionaldehyde showed that this process has a chain mechanism[33].

2. Formation of Acyl Radicals from Ketones

The most widely used method of generation of acyl radicals from ketones involves ultraviolet irradiation. Many studies have been made on the photolysis of ketones [29,34-38]. The mode of photolytic decomposition of ketones, like that of aldehydes, is greatly influenced by their structure. n-Alkyl methyl ketones, such as methyl propyl ketone and butyl methyl ketone undergo exclusively a type II decomposition on ultraviolet irradiation in the liquid phase, i.e. they decompose into acetone and an olefin (ethylene and propene respectively) [39]. Such decomposition (via a cyclic transition state) is readily undergone also by other ketones with hydrogen atoms in the γ-position. Acyl radicals are formed preferentially on ultravilet irradiation of aliphatic ketones without hydrogen atoms in the γ-position, for example, alkyl t-butyl ketones [39,40]. They are cleaved in accordance with the rule governing the formation of the most stable alkyl radical (in this case the t-butyl radical):

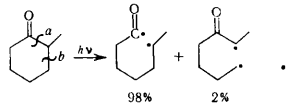
$$(CH_3)_3C-\overset{O}{\overset{\|}{C}}-R \xrightarrow{h\nu} (CH_3)_3C\cdot + O=\dot{C}-R.$$

Cis-trans isomerisation of hex-4-en-2-one also takes place with homolytic dissociation of the C–C bond adjoining the carbonyl group [41]. The $CH_3-\dot{C}=O$ radicals generated in this process add to the multiple bond (if the photolysis is carried out in the presence of an alkene) and butenyl radicals recombine to isomeric octadienes.

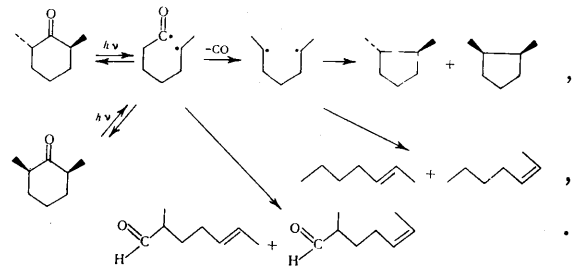
It has been shown that acyl radicals are obtained together with hydrogen and alkyl and α-oxoalkyl radicals in the liquid-phase radiolysis of simple aliphatic ketones (acetone [42], ethyl methyl ketone [43], and diethyl ketone [43]).

Many reactions are known in which cyclic ketones are photochemically cleaved with formation of an unsaturated aldehyde or ketone, which are formally products of an intramolecular disproportionation of intermediate acyl–alkyl biradicals. Nevertheless the problem of whether or not free radicals are really formed in the photolysis of cyclic ketones was regarded as controversial until recently [29]. In contrast to the free-radical mechanism, a hypothesis was put forward according to which the C–C bond of the cyclic ketone is dissociated and new bonds are formed by a synchronous mechanism, i.e. without the involvement of the radical pair [36,44].

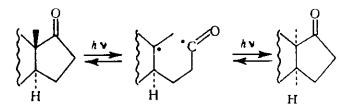
Nowadays the formation of an acyl–alkyl biradical on ultraviolet radiation should probably be regarded as proved, at least for simple cyclic ketones. Important studies designed to confirm this view have been made by Pritchard, Rickdorn, and others [45,46]. They found that the opening of the 2-methylcyclohexanone ring takes place to the extent of 98% at *a* and only to the extent of 2% at *b*. Such high process selectivity is due to the greater stability of a secondary alkyl radical compared with a primary radical:



As a result of the intramolecular disproportionation of the intermediate acyl–alkyl biradical, a mixture of *cis*- and *trans*-isomers of 5-heptenal is obtained (under the reaction conditions, these isomers are not interconverted) [49]. The photochemical cleavage of 2,6-dimethylcyclohexanone takes place similarly [45]. Ultraviolet irradiation of both the *cis*- and *trans*-isomer of this ketone leads to the same mixture of *cis*- and *trans*-1,2-dimethylcyclopentanones, *cis*- and *trans*-hept-2-enes, and *cis*- and *trans*-2-methylhept-5-enals with the same component ratio, which unambiguously demonstrates a free-radical mechanism:



2,3-Dimethylcyclopentanone is also cleaved by ultraviolet light with formation of an acyl-alkyl biradical, because the reaction products are a mixture of *cis*- and *trans*-1,2-dimethylcyclobutanes [47]. Homolytic dissociation of the C–C bond takes place also in the photolysis of bicyclic ketones, since examples of their photochemical epimerisation are known [48]:



Section V deals with examples of the migration of acyl groups, which confirm the free-radical mechanism of the photochemical cleavage of cyclic ketones. It should be noted that in some cases steric factors can favour the preferential occurrence of the reaction involving a molecular (synchronous) mechanism [49].

Radiolysis of cyclopentanone [50] leads to ring opening, probably via the same mechanism as in the photolysis of cyclic ketones, i.e. with intermediate formation of an acyl–alkyl biradical, but in this process side hydrogenation–dehydrogenation reactions play a significant role (the radiolysis products contain appreciable amounts of cyclopenten-2-one and cyclopentanol).

α-Diketones can also be used for the generation of acyl radicals. Thus diacetyl undergoes thermal dissociation into acetyl radicals with a 50% decomposition time of about 17 h at 145 °C [21]. Acetyl radicals are obtained from diacetyl also under milder conditions—when it is attacked by the alkyl radicals generated from the solvent by peroxides or ultraviolet irradiation [52,53]. In both cases intermediate α-oxoalkoxy-radicals are formed and are readily decomposed:

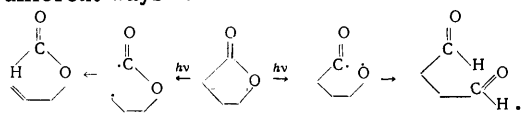
$$R\cdot + CH_3-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-CH_3 \rightleftarrows CH_3-\overset{\dot{O}}{\underset{R}{\overset{|}{C}}}-\overset{O}{\overset{\|}{C}}-CH_3 \rightarrow$$

$$\rightarrow CH_3-\overset{O}{\overset{\|}{C}}-R + CH_3-\dot{C}=O.$$

Photolysis of dibenzoyl leads to $C_6H_5-\dot{C}=O$ with a quantum yield of 0.25 on irradiation with light at a wavelength of 366 nm. [64] The photochemical cleavage of other α-diketones has also been investigated [55].

3. Formation of Acyl Radicals from Carboxylic Acid Derivatives

Irradiation of α-butyrolactone with light at a wavelength of 253.7 nm leads to the cleavage of the lactone ring in two different ways [56]:



The quantum yields of succinaldehyde and allyl formate are respectively 0.06 and 0.23 at 25°C. As a result of the photolysis of carboxylic α-ketoacids, carbon monoxide is evolved with formation of acyl and alkoxy-radicals [57].

A convenient method for the preparation of acyl radicals is based on the photolysis of *S*-acyl and *O*-alkyl xanthates [58]:

$$R-\overset{O}{\overset{\|}{C}}-S-\overset{S}{\overset{\|}{C}}OC_2H_5 \xrightarrow{h\nu} R-\dot{C}=O + \cdot S-\overset{S}{\overset{\|}{C}}OC_2H_5 .$$

Mixed benzoic and dithiocarbamic acid anhydrides can serve as a source of benzoyl radicals [59]:

$$R_2NC\overset{S}{\overset{\|}{S}}C\overset{O}{\overset{\|}{C}}C_6H_5 \xrightarrow[\lambda>3000\,Å]{h\nu} R_2N\overset{S}{\overset{\|}{C}}-S\cdot + O=\dot{C}C_6H_5 .$$

In contrast to *N*-disubstituted anhydrides, *N*-monosubstituted mixed anhydrides undergo photochemical dissociation in two ways [60]: with the scission of both $C_6H_5-\dot{C}=O$ and $C_6H_5C(O)\dot{S}$.

There are preliminary data [61] showing the formation of $R-\dot{C}=O$ on heating acid anhydrides with activated charcoal above 200°C. Schmidt [3,4,62,63] showed that acyl radicals are generated on ultraviolet irradiation of aliphatic and aromatic carboxylic acid halides:

$$R-C\overset{O}{\underset{X}{<}} \xrightarrow[2540\,Å]{h\nu} R-\dot{C}=O + X\cdot ,$$

where X = Br or Cl.

In contrast to the above reaction, when carboxylic acid halides react with peroxides, only the hydrogen atoms linked to the α-carbon atom of the acid halide are attacked; acyl radicals are not then formed [63,94].

Metal hydrides or carbonyls can be used successfully for the generation of acyl radicals from acid halides. For example, trialkyl- and triphenyl-tin hydrides readily react with acyl halides according to the mechanism [65]:

$$RCOCl + R'_3SnH \rightarrow R-\dot{C}=O + R'_3Sn\cdot + HCl ,$$

$$R'_3Sn\cdot + RCOCl \rightarrow R'_3SnCl + R-\dot{C}=O .$$

The relative reactivities of substituted aroyl halides in the reaction with tributyltin hydride have been determined [65]. The observed effect of substituents on the rate of removal of chlorine from the acid chloride is evidence of the important role of polar factors in the transition state

$$\left[ArC\overset{O}{\overset{\|}{}}\cdots Cl\cdots Sn \right]^{\cdot} .$$

C_2H_5COCl is approximately 5.6 times more reactive in the above reaction than C_6H_5COCl.

When perfluoroacyl chlorides react with nickel carbonyl, perfluoroacyl radicals are obtained [66]:

$$2\,R_FCOCl + Ni(CO)_4 \rightarrow 2\,R_F-\dot{C}=O + NiCl_2 + 4\,CO .$$

The reaction is catalysed by benzonitrile, the use of which as a solvent makes it possible to lower the temperature from 150° to 20°C.

Carboxylic acid chlorides are readily reduced to the corresponding aldehydes in the presence of palladium (Rosenmund reaction). Although the mechanism of this catalytic process is not altogether clear, it is quite likely that acyl radicals are formed in the first stage [67]:

$$2\,RCOCl + Pd \rightarrow 2R-\dot{C}=O + PdCl_2 .$$

4. Formation of Acyl Radicals from Other Compounds

Acyl radicals can be obtained by the addition of carbon monoxide to alkyl radicals generated by the usual methods from saturated and unsaturated hydrocarbons [68-72] or from tetra-alkyl-lead [73]:

$$R\cdot + CO \rightleftarrows R-\dot{C}=O .$$

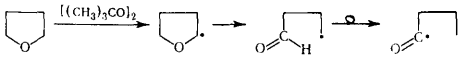
Since the reaction is reversible, the process is usually carried out under a pressure in excess of 500 atm in order to displace the equilibrium towards the formation of $R-\dot{C}=O$ and also to suppose the side reaction of R· with the solvent.

Thermolysis of α-acyl-t-alkyl hypochlorites leads to unstable α-acyl-t-alkoxy-radicals which are readily decomposed with elimination of $R-\dot{C}=O$:

$$R-\overset{O}{\overset{\|}{C}}-\overset{OCl}{\overset{|}{CR'_2}} \xrightarrow{(CCl_4)} R-\overset{O}{\overset{\|}{C}}-\overset{O\,\dot{}}{\overset{|}{CR'_2}} \rightarrow R-\dot{C}=O + R'COR' .$$

Subsequently the reaction develops as a chain process. The decomposition of α-acetyl-s-butyl hypochlorite results in a quantitative yield of 2-butanone and acetyl chloride [74].

Acyl radicals are obtained by the reaction of di-t-butyl peroxide with three-five-membered cyclic ethers, for example tetrahydrofuran (THF). [75] The reaction is remarkable because acyl radicals are generated as a result of an intramolecular rearrangement of the alkyl radicals formed initially [75]:



Attempts have been made to generate $R-\dot{C}=O$ radicals by the thermal decomposition of acyl and aroyl di-imides (RCO–N=N–COR). However, this process apparently has a complex mechanism, since propionyl di-imide initiates the polymerisation of olefins (acrylonitrile, styrene, etc.) only very slightly [73] and the thermal decomposition products of benzoyl di-imide contain only an insignificant amount of dibenzoyl [76]. More definite data supporting the formation of $C_6H_5-\dot{C}=O$ from benzoyl di-imide were obtained in a study of its photolytic cleavage [76].

III. ADDITION OF ACYL RADICALS TO MULTIPLE BONDS

1. GENERAL RELATIONS

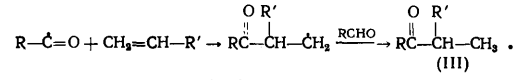
The free-radical addition of aldehydes to α-olefins was described for the first time by Kharasch et al. [1] The process has a chain mechanism:

$$RCHO \xrightarrow[(h\nu)]{peroxide} R-\dot{C}=O ,$$

$$R-\dot{C}=O + CH_2=CHR' \rightarrow \underset{(I)}{R\overset{O}{\overset{\|}{C}}CH_2-\dot{C}H-R'} + RCHO ,$$

$$I + RCHO \rightarrow \underset{(II)}{R\overset{O}{\overset{\|}{C}}CH_2CH_2R'} + R-\dot{C}=O \quad \text{etc.}$$

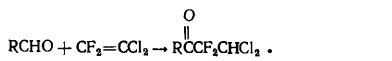
A detailed study of the products of the reaction initiated by peroxides [32,77], ultraviolet light [32], and γ-radiation [78,79] showed that acyl radicals attack not only the terminal but partly also the β-carbon atom of the vinyl group in the α-olefin:



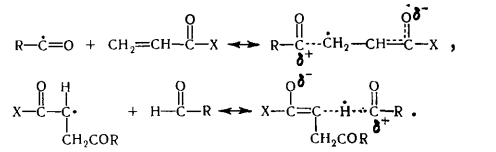
The content of compound (III) in a mixture of compounds (II) and (III) is 5–10%. The composition of the mixture of isomeric ketones is independent of the method of initiation of the reaction and of the reactant ratio [32].

As in other free-radical reactions, the mode of addition of R–Ċ=O to olefins is determined in the first place by the degree of stabilisation of the intermediate alkyl radical. The addition to isobutene [32] and 2-methylbut-2-ene [80] takes place almost exclusively at the least substituted carbon atom of the C=C group and the addition to straight-chain alk-2-enes takes place approximately equally at both carbon atoms linked by the double bond [80].

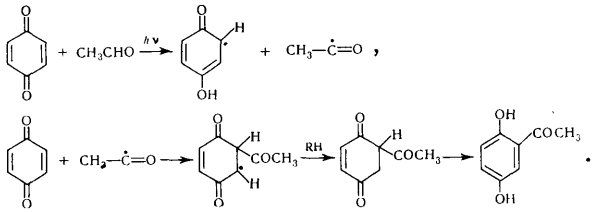
The radical additionof aldehydes to norbornene and camphene takes place stereoselectively with formation of ketones having the *exo*- and *endo*-configurations respectively [81,82]. When acyl radicals react with $\alpha\beta$-unsaturated acids, their esters, and nitriles, the β-carbon atom of the above compounds is also attacked preferentially. The reaction of aliphatic aldehydes with asymmetric dichlorodifluoroethylene gives only one isomer [83]:



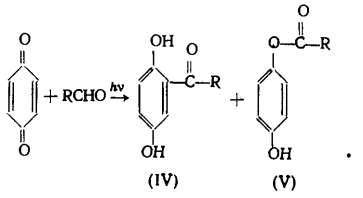
Although the reactivities of acyl radicals with respect to different types of double bond have not been estimated quantitatively, it has been shown in many cases that they add most readily to >C=C< or >C=O bonds with a reduced electron density. The radical addition of aldehydes to $\alpha\beta$-unsaturated carbonyl compounds and nitriles, perfluoro-olefins, and hexafluoroacetone takes place with a high yield and without the formation of an appreciable amount of telomers. According to Walling's hypothesis [84], the nucleophilic properties of acyl radicals are due to the effect of their electron-donating properties in the transition state in stages involving addition and chain transfer:



The role of polar factors in the attack by acyl radicals on multiple bonds is shown most strikingly in the photoinitiated reaction of aldehydes with quinones. When a solution of 1,4-benzoquinone in acetaldehyde is illuminated, hydroquinone (15%), acetylhydroquinone (67%), and an insignificant amount (0.6%) of *p*-hydroxyphenyl acetate are obtained [85]. The mechanism of the formation of acetylhydroquinone may be as follows:

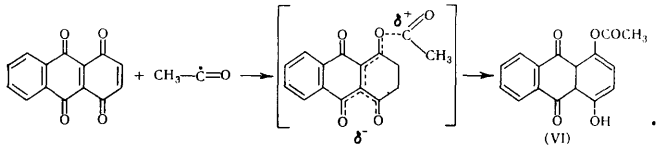


The products of the addition of benzaldehyde to benzoquinone contain benzoylhydroquinone (49%) and hydroquinone monobenzoate (15%), i.e. benzoyl radicals add not only to the carbon–carbon double bond but also attack to an appreciable extent the carbonyl group of the quinone [86]. The lower selectivity of the addition of benzaldehyde compared with acetaldehyde is probably associated with the fact that C_6H_5–Ċ=O is less nucleophilic than CH_3–Ċ=O owing to the conjugation of the unpaired electron with the benzene ring. The ratio of the products of the addition of substituted benzaldehydes to the >C=C< and >C=O bonds of benzoquinone depends greatly on the nature of the substituent:



The (V) : (IV) ratio increases as the R–Ċ=O radical becomes less nucleophilic, *p*-nitrobenzaldehyde and cinnamaldehyde adding exclusively to the carbonyl group of benzoquinone [86].

When a solution of quinizarinquinone in acetaldehyde is illuminated, only the monoester is obtained [86], which can be explained by the ease of formation of the transitional dipolar structure promoting attack on the oxygen atom of the carbonyl group by the acetyl radical:



In contrast to the reaction of acetaldehyde with unsubstituted *p*-benzoquinone, its addition to chloranil takes place almost exclusively at the carbonyl group [87], owing to steric hindrance in the attack on the C=C bond of chloranil.

The reactivities of chloroperfluoro-olefins in the homolytic reaction with aldehydes decrease in the sequence $CFCl{=}CCl_2 > CF_2{=}CCl_2 > CFCl{=}CFCl$. [88]

The relative reactivities of cyclic olefins in their radical reaction with acetaldehydes initiated by γ-radiation have been determined [89]: cyclo-octene > cyclopentene > cycloheptene > cyclohexene.

2. ADDITION TO THE CARBON–CARBON DOUBLE BOND

In recent years the addition of aldehydes to olefins has come to be very widely used, since it permits the ready synthesis of a wide variety of organic compounds containing the keto-group [18,90,91]. It is usually initiated by organic peroxides, ultraviolet light, or γ-radiation. It has been shown recently that oxygen and variable-valence metal salts can also be employed as initiators. Each of the above methods of initiation has its characteristics, which have a specific effect on the process. Therefore the examples of the addition of R–Ċ=O to the carbon–carbon double bond will be classified on the basis of the methods of initiation of the reaction.

a. Reactions Initiated by Peroxides

The addition of aldehydes to olefins is usually initiated by benzoyl and acetyl peroxides, which undergo thermal decomposition at 80–100°C. It is undesirable to carry out the reaction above 100°C since decarbonylation of acyl radicals begins to play an important role under these conditions (Section IV). In order to suppress the telomerisation side reaction, a three–five-fold excess of the aldehyde is employed.

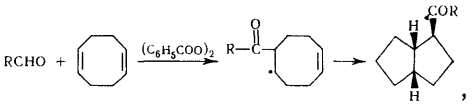
The free-radical addition of aldehydes to ethylene [92], alk-1-enes [1,32,77,93–95], α-pinene [97], β-pinene [77,97], camphene [81,97], norbornene [81,82], (+)-limonene [97], cyclohexene [93], crotonic [98] and substituted acrylic [99] acids and their esters [98,100] and nitriles [99,101], the nitrile of cinnamic acid [98,102], the esters of maleic [98,100,103–105], fumaric [103], itaconic [103], aconitic [108], and undeconoic [100,106–108] acids, αβ-unsaturated ketones [109,110], allyl acetate [111,112], and other esters of allyl alcohols [112,113], allyl ethers [112], acetals of acrolein [112,114], dichlorodifluoroethylenes [83], perfluoro-olefins [115,116], and unsaturated silicon-containing compounds [117–119] has been described.

The radical addition of butyraldehyde to 3,3-diphenylbut-1-ene is accompanied by a rearrangement with migration of the phenyl group [120]:

$$R\dot{C}{=}O + CH_3C(C_6H_5)_2CH{=}CH_2 \longrightarrow$$

$$CH_3C(C_6H_5)_2\dot{C}HCH_2COR \xrightarrow{O} CH_3\dot{C}(C_6H_5)CH(C_6H_5)CH_2COR$$

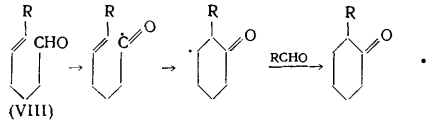
In the presence of benzoyl peroxide a bicyclic ketone is formed from aliphatic aldehydes and *cis-cis*-cyclo-octa-1,5-diene by an intramolecular interaction in the intermediate cycloalkyl radical with the second double bond [121]:



where R = CH_3 or C_3H_7.

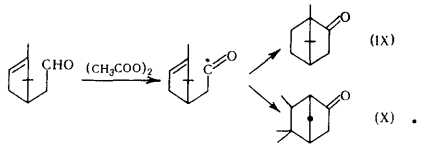
According to patent data, acetaldehyde adds to hexa-1,5-diene [93] and isoprene [122] (in both cases to one double bond).

The acyl radicals generated from unsaturated aldehydes of type (VIII) add intramolecularly to the double bond, forming a six-membered cyclic ketone (yield 40 to 50%):[123]



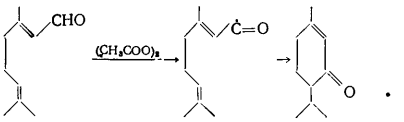
(VIII)

The free-radical cyclisation of α-campholenic aldehyde [124] takes place in two ways:



The reaction products consist of a mixture of 95% of camphor (IX) and 5% of dihydrocamphenone (X).

Similar results were obtained in a study of the radical cyclisation of apocampholenic aldehyde, citronellal, and citral [125]. For the last aldehyde, the reaction is complicated by the simultaneously occurring thermal isomerisation processes, but on rapid decomposition of acetyl peroxide in citral an αβ-unsaturated cyclic ketone is the main product:

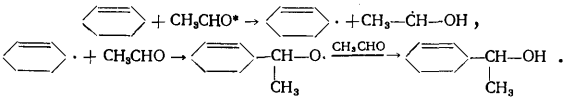


In contrast to the reactions described above, the interaction of 4-formylcyclohexene and *endo*-5-formylbicyclo-[2,2,2]oct-2-ene with di-t-butyl peroxide leads to dimeric products [126].

b. Reactions Initiated by Ultraviolet Light, γ-Radiation, and β-Radiation

The radiation and photochemical methods for the initiation of the reactions of aldehydes with olefins have been fairly well investigated. The addition of aldehydes to ethylene [127,128], propene [78,127], isobutene [127,129], alk-1-enes [79,80,127], alk-2-enes [80,127], cyclohexene [79,130,131], other cyclic mono-olefins [85], chlorotrifluoroethylenes [84,132], perfluorocyclobutene [116], and dimethyl esters of maleic and fumaric acids [133] has been achieved under the influence of γ-radiation.

In the reaction of aldehydes with olefins initiated by ultraviolet light the main process is often accompanied by side reactions, which as a rule play a significant role. Thus the photochemical addition of butyraldehyde to hept-1-ene proved to be relatively ineffective owing to the formation of a considerable amount of parabutyraldehyde [32]. The photochemical reaction of aliphatic aldehydes with cycloalkenes also does not take place unambiguously [130]: a considerable amount of acetoin was obtained together with cyclohexyl methyl ketone from a mixture of acetaldehyde and cyclohexane. According to the data of other workers [134], cyclohexylmethylmethanol is also formed in the above reaction, probably according to the following mechanism:



Illumination of an equimolar mixture of methylenecyclohexane and n-butyraldehyde gives four products, one of which is cyclohexylmethyl ethyl ketone [135].

A preparative method of synthesising γ-silylketones by the photochemical addition of aldehydes to vinylsilanes has been proposed [136]:

$$R_3SiCH{=}CH_2 + R'CHO \xrightarrow{h\nu} R_3SiCH_2CH_2\overset{O}{\overset{\|}{C}}R' ,$$

where R = CH_3, C_2H_5, or OC_2H_5 and R′ = CH_3, C_2H_5, iso-C_4H_9, etc. Benzaldehyde does not react with vinylsilanes [136].

Only one example of the initiation of the addition reaction by a beam of electrons has been described. When a mixture of acetaldehyde and cyclohexene was exposed to β-radiation, cyclohexyl methyl ketone and a considerable amount of side products—acetoin and 1-acetyl-2-(2′-cyclohexenyl)cyclohexene—were obtained [130].

c. Reactions Initiated by Oxygen and (or) Variable-valence Metal Salts

The effectiveness of oxygen as an initiator of the addition of aldehydes to a multiple bond depends on the structure of the olefin. The reaction takes place most readily with olefins having an electrophilic multiple bond. Thus the ester of butyrylsuccinic acid was obtained from butyraldehyde and dimethyl maleate in a quantitative yield [137]. The process is interesting because acyl radicals are generated directly in the reaction between the aldehyde and oxygen (the intermediate peroxides do not play a significant role in this case):

$$RCHO + O_2 \rightarrow R-\dot{C}=O + HO\dot{O} \text{ or}$$

$$2\,RCHO + O_2 \rightarrow 2R-\dot{C}=O + H_2O_2\ ,$$

$$R-\dot{C}=O + CH_3OOCCH=CHCOOCH_3 \xrightarrow{RCHO} H_3COOC\underset{\displaystyle COR}{\underset{|}{C}}HCH_2COOCH_3\ .$$

In contrast to this reaction, the oxygen-initiated addition of aldehydes to alk-1-enes leads to the formation of large amounts of acids [32]. However, the process selectivity increases sharply when acetic anhydride is introduced into the system [138,139]. Its role consists in the binding of the peracid, arising in the oxidation of the aldehyde, into a diacyl peroxide. The peroxide obtained *in situ* subsequently undergoes thermal decomposition into free radicals and thus initiates the reaction [139]

$$RCHO \xrightarrow{O_2} R-\overset{\displaystyle O}{\overset{\|}{C}}-OOH\ ,$$

$$R-\overset{\displaystyle O}{\overset{\|}{C}}-OOH + (CH_3CO)_2O \rightarrow R-\overset{\displaystyle O}{\overset{\|}{C}}-O-O-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3 + CH_3COOH$$

$$\downarrow$$

$$R\cdot + 2\,CO_2 + \cdot CH_3\ .$$

The products of the addition of aldehydes to olefins initiated by oxygen in the presence of acetic anhydride are formed in yields up to 90% with a comparatively low degree of oxidation of the aldehyde to the acid (5–10%).

The use of oxygen in the presence of catalytic amounts of cobalt salts proved to be even more effective [96,137]. The method of oxidative catalytic initiation has been used to synthesise various ketones and their functional derivatives [96,137,140,141]. The preparation in a single stage of γ-acetylpropyl acetate [141]—one of the starting materials in the manufacture of vitamin B_1—may be of particular practical interest [141]:

$$CH_3CHO + CH_2=CHCH_2OOCCH_3 \xrightarrow[Co(OOCCH_3)_2]{O_2} CH_3\overset{\displaystyle O}{\overset{\|}{C}}CH_2CH_2CH_2OOCCH_3\ .$$

This and other similar reactions take place readily at room temperature.

The oxidation of aldehydes by oxygen is a complex chain process. In order to determine at which stages acyl radicals are generated, the structures of the intermediate peroxides [142] and the kinetics and mechanisms of their thermal [143] and catalytic [19] decomposition were investigated.

Variable-valence metal salts, for example manganese(III) triacetate, can initiate the addition of aldehydes to a multiple bond also in the absence of oxygen [27,28].

3. ADDITION TO A CARBON–CARBON TRIPLE BOND

Only a few examples of the addition of acyl radicals to a C≡C bond are known [133,144]. The reaction of acetaldehyde with acetylene in the presence of benzoyl peroxide takes place in steps according to the mechanism [144]:

$$CH_3CHO \rightarrow CH_3-\dot{C}=O \xrightarrow{CH\equiv CH} CH_3COCH=\dot{C}H \xrightarrow{CH_3CHO} CH_3COCH=CH_2 \xrightarrow{CH_3\dot{C}=O} \rightarrow$$

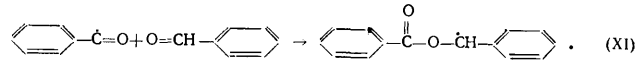
$$\rightarrow CH_3CO\dot{C}HCH_2COCH_3 \xrightarrow{CH_3CHO} CH_3COCH_2CH_2COCH_3\ .$$

γ-Diketones are formed also as a result of the radical addition of aldehydes to butylacetylene [144] and acetylenedicarboxylic acid [133].

4. ADDITION TO A $\rangle C=O$ BOND

Addition to a carbonyl group is less typical for acyl radicals than addition to a carbon–carbon double bond. On the basis of the available data, it is impossible to arrive at any general conclusions concerning the factors which determine the capacity of acyl radicals to attack the $\rangle C=O$ group in each specific case. The activity of the $R-\dot{C}=O$ radicals depends most on the nature of R and the structure of the carbonyl compound (see above).

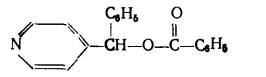
When organic peroxides are decomposed in benzaldehyde, the intermediate benzoyl radicals readily add to the carbonyl group of the aldehyde [145,146]:



(XI)

The radicals (XI) subsequently recombine. A similar reaction occurs also with *o*-methylbenzoyl radicals generated from *o*-methylbenzaldehyde [147].

The interaction of benzaldehyde with a peroxide in the presence of pyridine yields compound (XII), which is formally a product of the addition of radical (XI) to pyridine [148]:



(XII)

The decomposition of di-t-butyl peroxide in 2,3-dimethyl-3-phenylbutanal gives preferentially an ester owing to the addition of an acyl radical to the carbonyl group of the aldehyde with subsequent chain transfer [149]:

$$R-\dot{C}=O + RCHO \rightarrow RCOO-\dot{C}H-R \xrightarrow{RCHO} RCOOCH_2R\ .$$

The free-radical addition of benzaldehyde and aliphatic aldehydes to hexafluoroacetone and chlorofluoro-derivatives of acetone takes place very readily [150]:

$$RCHO \xrightarrow{\text{initiator}} R-\dot{C}=O$$

$$R-\dot{C}=O + O=\overset{\displaystyle CX_3}{\overset{|}{C}}-\underset{\displaystyle CX_3}{\underset{|}{}} \rightarrow RCO-\overset{\displaystyle O}{\overset{\|}{C}}-\overset{\displaystyle CX_3}{\overset{|}{C}}\cdot \xrightarrow{RCHO} RCO-\overset{\displaystyle O}{\overset{\|}{C}}-\overset{\displaystyle CX_3}{\overset{|}{C}}H\ ,$$

$$\qquad\qquad\qquad

of tributyltin hydride was proposed recently. The reaction takes place at room temperature via a chain mechanism:

$$RCOCl \xrightarrow{Bu_3SnH} R-\dot{C}=O\,,$$

$$R-\dot{C}=O + R'R''C=O \rightarrow RCOO-\dot{C}R'-R''\,,$$

$$RCOO-\dot{C}R'-R'' + Bu_3SnH \rightarrow RCOOCHR'R'' + Bu_3Sn\cdot\,,$$

$$Bu_3Sn\cdot + RCOCl \rightarrow Bu_3SnCl + R-\dot{C}=O \quad \text{etc.}\,.$$

The relative reactivities of various aldehydes and ketones with respect to the propionyl radical have been determined. It was found that n-heptanal is more reactive than benzaldehyde and the rate of addition of $CH_3CH_2-\dot{C}=O$ to cyclohexanone is about 20 times faster than the rate of addition of cyclopentanone [151].

The relative reactivities of substituted benzaldehydes in the above reaction are correlated with the σ^+ constants [151]. Electron-accepting substituents accelerate and electron-donating substituents retard the reaction (ρ = 0.43), which is consistent with the hypothesis that acyl radicals have nucleophilic properties.

An ester can be synthesised also by the direct interaction of an acid chloride or bromide with a substituted tin hydride [151,153]. Benzyl benzoate was obtained by this method in 87% yield from benzoyl chloride and triphenyltin hydride at room temperature in the absence of a solvent [153]:

$$2\,C_6H_5COCl + 2\,(C_6H_5)_3SnH \rightarrow C_6H_5COOCH_2C_6H_5 + 2\,(C_6H_5)_3SnCl\,.$$

It has been suggested that in this case an aldehyde formed as an intermediate in the reduction of the acid chloride is acylated [151]. This explanation is consistent with the finding that an aldehyde is present in the reaction product and the aldehyde : ester ratio varies from 9 to 0.25, depending on the nature of the reactants and the experimental conditions [151]. The ester is probably formed by the radical-chain mechanism described above, since the reaction is sensitive to inhibitors and is accelerated by azobisisobutyronitrile [153].

Esters of enediols have been synthesised by the reaction of perfluoroacyl chlorides with nickel carbonyl in benzonitrile:

$$R_FCOCl \xrightarrow{Ni(CO)_4} 2\,R_F-\dot{C}=O \rightarrow R_F-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-R_F;$$

$$R_F-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-R_F + R_F-\dot{C}=O \rightarrow R_F\overset{O}{\overset{\|}{C}}O-\overset{R_F}{\overset{|}{C}}=\overset{R_F}{\overset{|}{C}}-O\cdot \xrightarrow{R_F-\dot{C}=O} R_F\overset{O}{\overset{\|}{C}}O\overset{R_F}{\overset{|}{C}}=\overset{R_F}{\overset{|}{C}}\overset{O}{\overset{\|}{C}}O-R_F.$$

The addition of an acyl radical to the carbonyl group probably takes place as one of the stages in the original method for the preparation of substituted propiolactones by the condensation of aldehydes with keten under the influence of benzoyl peroxide [154]:

$$R-\dot{C}=O + CH_2=C=O \rightarrow \overset{R-C=O}{\overset{|}{CH_2}}-\dot{C}=O \rightarrow \overset{\dot{R}-C-O}{\overset{|}{CH_2}}-C=O \xrightarrow{RCHO} \overset{R-CH-O}{\overset{|}{CH_2}}-C=O.$$

9-Benzoyloxy-10-hydroxyphenanthrene was obtained by a photochemical reaction of benzaldehyde with phenanthrenequinone [155]:

$$C_{14}H_8\langle{}^{O}_{O} \xrightarrow{h\nu} C_{14}H_8\langle{}^{O\cdot}_{O\cdot}\,,$$

$$C_{14}H_8\langle{}^{O\cdot}_{O\cdot} + C_6H_5CHO \rightarrow C_{14}H_8\langle{}^{OH}_{O\cdot} + C_6H_5-\dot{C}=O\,,$$

$$C_6H_5\dot{C}=O + C_{14}H_8\langle{}^{O}_{O} \rightarrow C_{14}H_8\langle{}^{O\cdot}_{OCOC_6H_5} \xrightarrow{C_6H_5CHO} C_{14}H_8\langle{}^{OH}_{OCOC_6H_5}\,.$$

5. Addition to N=O and N=N Bonds

The addition of acyl radicals to N=O and N=N bonds has been much less investigated than the addition to C=C and C=O bonds.

The reaction of acyl radicals with nitroso-compounds [156] is of interest as a convenient method for the synthesis of stable nitroxy-radicals:

$$R-\dot{C}=O + O=N-R' \rightarrow R-\overset{O}{\overset{\|}{C}}-\overset{R'}{\overset{|}{N}}-O\,.$$

t-Butyl peroxide and also nitrosoalkanes, which readily decompose into NO and alkyl radicals under the influence of heat or ultraviolet light, were used to generate $R-\dot{C}=O$ radicals in this process. Stable acylnitroxy-radicals were obtained also by another method [156]—by decomposing alkyl nitrites in hydrocarbons. The aldehydes and nitroso-compounds formed as intermediates react further with one another as described above.

A radical-chain addition of aldehydes to certain azo-compounds (azobenzene, azodibenzoyl, and azodicarboxylic acid esters) has been described:

$$RCHO + R'-N=N-R' \rightarrow R-\overset{O}{\overset{\|}{C}}-\overset{R'}{\overset{|}{N}}-NH-R'\,,$$

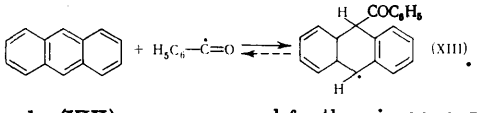
where R = C_6H_5CO, CH_3CO, etc. and R′ = C_6H_5, C_6H_5CO, or R″OCO. Di-t-butyl peroxide [157], azobisisobutyronitrile [158], and atmospheric oxygen [159,160] were used as initiators. The reaction is of preparative interest for the synthesis of acylated hydrazine derivatives (yields up to 90%).

In its thermal and photolytic decomposition in organic solvents, azodibenzoyl undergoes radical benzoylation [79], which leads to tribenzoylhydrazine and diphenyloxadiazole. The same compounds were isolated in the oxidation of benzoylhydrazine by silver oxide [76]. Both reactions probably have similar mechanisms. It has been suggested [76] that in the latter case benzoyl radicals add to the benzoylhydrazine formed.

Benzoyl radicals can also attack the azo-group of azobisisobutyronitrile [157].

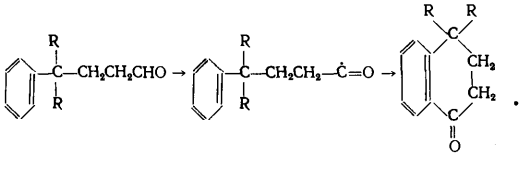
6. ADDITION TO AROMATIC SYSTEMS

Very little is still known about the addition of acyl radicals to aromatic systems. The addition of the benzoyl radical to anthracene has been investigated [161]. The first stage of this process is probably reversible:



The radicals (XIII) are consumed further in several ways: they recombine with one another or with $C_6H_5-\dot{C}=O$; also they lose hydrogen atoms and are converted into benzoylanthracene.

When a peroxide is allowed to react with aliphatic aldehydes containing a phenyl substituent in the γ-position, the benzene ring undergoes intramolecular acylation [149]:



The oxidation of benzoylhydrazine by silver(II) oxide in the presence of ferrocene leads to benzoylferrocene. It is most likely that ferrocene is acylated by a free-radical mechanism [161,162].

The possibility of the free-radical acylation of heterocyclic bases (pyridine, acridine, isoquinoline, etc.) by aldehydes in an acid aqueous medium has been demonstrated [163]. The reaction is initiated by redox systems. Owing to the nucleophilic properties of acyl radicals, they readily attack the electrophilic centres in the rings of the above bases.

IV. DECARBONYLATION

Decarbonylation is the reverse process in relation to the addition of carbon monoxide to alkyl radicals described in Section II:

$$R-\dot{C}=O \rightleftarrows R' + CO.$$

At a pressure close to atmospheric R–Ċ=O decomposes almost irreversibly and therefore such decomposition is often used as a method for the generation of free alkyl radicals [26]. Acyl radicals are usually obtained from aldehydes. The decarbonylation of aldehydes is a chain process:

$$RCHO + Z\cdot \rightarrow R-\dot{C}=O+ZH,$$

$$R-\dot{C}=O \rightarrow R' + CO,$$

$$RCHO + R\cdot \rightarrow RH + R-\dot{C}=O \text{ etc.}$$

The ease of removal of CO from R–Ċ=O depends significantly on the nature of R· (Table 2). It has been firmly established in a number of cases that the decomposition of R–Ċ=O takes place more readily the more stable is R. [16,126,164,165] However, this rule is valid only for aliphatic and alicyclic acyl radicals (benzoyl radicals do not show any capacity for the removal of CO) [4,16,58].

Table 2. Relative reactivities of certain aldehydes in the decarbonylation reaction [164].

R in RCHO	Reactivity	R in RCHO	Reactivity
$CH_3CH_2CH_2$	1	1-norbornyl	0.6
$(CH_3)_2CH$	8.3	1-bicyclo[2,2,2]octyl	110
$(CH_3)_3C$	90	1-adamantyl	175

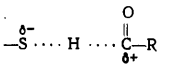
The rate of decarbonylation of the first three aldehydes depends linearly on the R–H bond energy in the hydrocarbon formed. The C–H bond energies in norbornane, bicyclo[2,2,2]octane, and adamantane have been estimated by extrapolation on the basis of the above relation [164].

The stability of the intermediate alkyl radical evidently plays a decisive role also in the decarbonylation of cyclopropanealdehyde [165] (Table 3).

The decarbonylation of the optically active bicyclo[2,2,2]octanealdehyde gave a racemic mixture of bicyclooctanes [166].

In a series of bicyclic aldehydes with similar structures, *endo*-bicyclo[2,2,2]oct-2-ene-5-aldehyde is decarbonylated most readily owing to the formation, following the removal of CO, of a stable non-classical alkyl radical [126]. The reactivities of alicyclic [167,168] and bicyclic [126] aldehydes are in many cases significantly influenced by steric factors.

The dependence of the decarbonylation chain length on the proportions of the aldehyde and di-t-butyl peroxide [169], usually employed as an initiator, has been investigated. In the presence of small amounts of mercaptans the chain length increases appreciably [170–172]. The explanation is that the formation of the transition state S...H...C requires a lower activation energy than the formation of the transition state C...H...C, owing to the ease of formation of the acylated complex



Thus mercaptans play the role of chain-transfer agents in the decarbonylation of aldehydes.

Table 3.

Aldehyde			
Yield of CO, %	traces	50	90

The decomposition of acyl radicals is widely used for the investigation of various reactions of the radicals produced in this process. The following types of rearrangement of alkyl radicals have been observed in the decarbonylation of aldehydes: 1,2-C,C- [166,173–182] and 1,3-C,C-migration [149] of aryl groups, 1,2-C,C-migration of the acetoxy-group [183], allyl rearrangement [184], ring opening [182], and ring expansion [185,186]. Attempts have also been made to observe the 1,2-C,C-migration of methyl [187], benzyl [188], and phenoxy-groups [178] and 1,2-S,C-migration of the phenyl group [189], but these were unsuccessful.

The alkyl radicals formed in the decarbonylation of aldehydes are not only capable of removing hydrogen atoms but some can also add to the aldehyde groups:

$$RCHO \xrightarrow{-H\cdot} R-\dot{C}=O \xrightarrow{-CO} R,$$

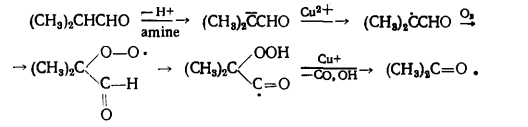
$$R\cdot + RCHO \rightarrow R_2CH-O,$$

$$R_2CH-O\cdot + RCHO \rightarrow R_2CHOH + R-\dot{C}=O \text{ etc.}$$

The decomposition of di-t-butyl peroxide in n-butyraldehyde yields propane and dipropylmethanol in proportions of about 10 : 1. [190]

In the decarbonylation of aldehydes in the presence of olefins (alk-1-enes [191], chloropolyfluoroethylenes [83], and diethylmaleate [192]), the addition of alkyl radicals to the multiple bond was observed.

A convenient method has been proposed for the synthesis of ketones [193] by the oxidation of α-branched aldehydes with oxygen in a polar solvent (dimethylformamide, t-butyl alcohol). The ketone is formed as a result of the decomposition of the intermediate α-hydroperoxyacyl radical:

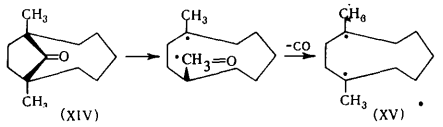


The reaction is catalysed by copper salts and tertiary amines {amines with a sterically hindered electron pair

at the nitrogen atom, for example 1,4-diazabicyclo-[2,2,2]octane, are the most effective}.

The mechanism of the decarbonylation reactions of aldehydes and ketones initiated by ultraviolet radiation is frequently not susceptible to unambiguous interpretation, since the homolytic dissociation of the C–C bond and the removal of CO can occur as two consecutive stages or in a single photochemical step without the intermediate formation of an acyl radical. However, since the decarbonylation processes initiated by peroxides and ultraviolet radiation have many features in common, in many cases preference is given to the mechanism involving the R–Ċ=O radical. This hypothesis is valid at least for photochemical reactions of acyclic and simple cyclic ketones.

Since photolytic reactions in solution are usually carried out under mild conditions, only the least stable acyl radicals readily undergo photochemical decarbonylation. For example, acyl radicals with a quaternary α-carbon atom readily lose carbon monoxide [194,195]. Photolysis of the bicyclic ketone (XIV) [194] leads to three isomeric olefins as a result of an intramolecular disproportionation of the intermediate biradical (XV):



(XIV) (XV)

In the photolysis of dibenzyl ketone [196], carbon monoxide is split off and the benzyl radicals recombine quantitatively:

$$C_6H_5CH_2\overset{O}{\overset{\|}{C}}CH_2C_6H_5 \xrightarrow{h\nu} 2C_6H_5CH_2\cdot + CO,$$
$$2\,C_6H_5CH_2\cdot \rightarrow C_6H_5CH_2CH_2C_6H_5.$$

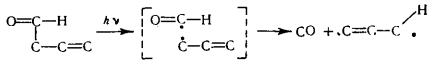
The free-radical mechanism of this reaction is confirmed by the fact that, when a mixture of dibenzyl ketone and 1,1,3,3-tetraphenylacetone is irradiated, two symmetrical and one asymmetric hydrocarbon are formed as a result of the recombination of the corresponding arylalkyl radicals.

In contrast to acetone, which hardly undergoes photolysis in the liquid phase [40,197], monochloropentafluoroacetone decomposes under the influence of ultraviolet light with liberation of carbon monoxide [198]. This is evidence of the instability of the CF_3–Ċ=O and CF_2Cl–Ċ=O radicals.

The liquid-phase photolysis of aldehydes, particularly those branched at the α-carbon atom, also gives rise to the elimination of carbon monoxide. Photochemical decarbonylation is inhibited by hydroquinone, which is evidence of a chain mechanism of the process [199]. The primary step in the photochemical decomposition of unsaturated aldehydes with a quaternary α-carbon atom yields formyl and alkyl radicals. The latter remove a hydrogen atom from the solvent and H–Ċ=O undergoes further decomposition [200]:

$$RCHO \xrightarrow{h\nu} RCHO^* \rightarrow R\cdot + H\text{–}\dot{C}{=}O$$
$$\text{solvent} \rightarrow RH \qquad \rightarrow CO.$$

The mechanism of the decarbonylation of $\beta\gamma$-unsaturated aldehydes differs from that described above. Hydrogen transfer in such aldehydes takes place intramolecularly via a stage involving the formation of a radical pair or via a synchronous mechanism [200,201]:



In the photolysis of benzaldehyde a certain amount of carbon monoxide is given off; however, this is not due to the decomposition of C_6H_5–Ċ=O, but is probably a result of the decomposition of the intermediate keten [4].

The irradiation of *O*-alkyl and *S*-acyl xanthates with visible or ultraviolet light [58] also leads to the liberation of carbon monoxide, which is believed to be caused by the decomposition of acyl radicals:

$$R\text{–}\overset{O}{\overset{\|}{C}}\text{–}S\text{–}\overset{S}{\overset{\|}{C}}\text{–}OC_2H_5 \xrightarrow{h\nu} R\text{–}\overset{S}{\overset{\|}{\dot{C}}}{=}O + \cdot S\text{–}\overset{S}{\overset{\|}{C}}\text{–}OC_2H_5,$$
$$R\text{–}\overset{S}{\overset{\|}{\dot{C}}}{=}O \xrightarrow{-CO} R\cdot;\ R\cdot + \cdot S\text{–}\overset{S}{\overset{\|}{C}}\text{–}OC_2H_5 \rightarrow R\text{–}S\text{–}\overset{S}{\overset{\|}{C}}\text{–}OC_2H_5.$$

The reaction takes place smoothly when R = benzyl, s-alkyl, or t-alkyl, is more difficult with acyl xanthates where R is a primary alkyl, and does not occur in the photolysis of *S*-benzoyl xanthate.

Trimethylacetaldehyde undergoes a radical-chain decarbonylation in oxidation by manganese(III) acetate [27], as under the influence of peroxides or ultraviolet light. The intermediate t-butyl radicals remove hydrogen from the aldehyde and are also oxidised by the manganese(III) salt to isobutene:

$$(CH_3)_3CCHO \xrightarrow{Mn(OOCCH_3)_3} (CH_3)_3C\text{–}\dot{C}{=}O \rightarrow (CH_3)_3C\cdot + CO$$
$$\text{aldehyde} \rightarrow (CH_3)_3CH \qquad Mn^{III} \rightarrow CH_2{=}C(CH_3)_2.$$

In the oxidation of triphenylacetaldehyde with chromic acid [202], the evolution of carbon monoxide was also observed:

$$(C_6H_5)_3CCHO + Cr^{IV} \rightarrow (C_6H_5)_3C\text{–}\dot{C}{=}O + Cr^{III} + H^+,$$
$$(C_6H_5)_3C\text{–}\dot{C}{=}O \xrightarrow[H_2O]{Cr^{IV}(Cr^{VI})} (C_6H_5)_3COH + CO.$$

The reaction products contain (apart from triphenylmethanol) triphenylacetic acid, which may be formed as a result of the oxidation of the intermediate acyl radical with electron transfer or as a result of two-electron oxidation of the initial aldehyde. A more selective decarbonylation of $(C_6H_5)_3CCHO$ was observed when chromyl acetate or cerium(IV) salts were used as oxidising agents (in these cases the reaction products did not contain triphenylacetic acid) [202].

The decarbonylation of β-phylisovaleraldehyde catalysed by palladium [203] results in the formation of only an insignificant amount of the neophyl rearrangement products of this aldehyde. The authors believe that the decarbonylation may have a radical mechanism, but, as a result of the fixation of the radicals on the surface of the catalyst, the migration of the phenyl group in the 2-methyl-2-phenylpropyl radical is difficult.

V. PHOTOCHEMICAL ACYL RADICAL MIGRATION PROCESSES

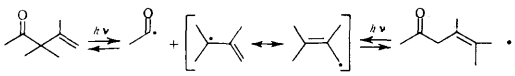
Many photochemical rearrangements of ketones, esters, and carboxylic acid amides involve the migration of acyl radicals. The rearrangements of ketones with

different structures (aliphatic, mono-, bi-, and polycyclic, $\beta\gamma$-unsaturated, etc.) have been thoroughly investigated.

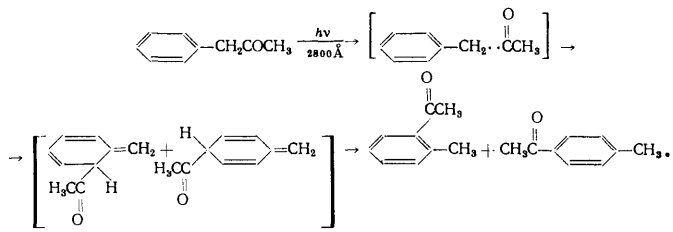
1. C,C-MIGRATION

a. Rearrangement of $\beta\gamma$-Unsaturated Acyclic Ketones

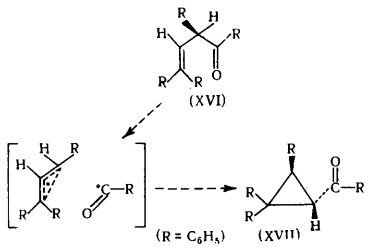
Kiefer and Carlson[204] observed the allyl rearrangement of 2,3,3-trimethylpent-1-en-4-one via a free-radical mechanism:



Irradiation of benzyl methyl ketone in t-butyl alcohol or n-hexane causes the formation of a mixture of *o*- and *p*-methylacetophenones[205]. The photolysis products also contain dibenzyl. The ratio of methylacetophenone and dibenzyl increases as the concentration of the ketone falls. The following mechanism has been proposed for this reaction:



When the ketone (XVI) is irradiated with ultraviolet light in benzene, the benzoyl group migrates with formation of the cyclopropane ring[206]. The reaction is stereospecific. However, cyclisation is not the main process in the photolysis of compound (XVI): it largely undergoes fragmentation to phenylallyl radicals, which then recombine, and benzoyl radicals, which probably behave as precursors of biphenyl. Compound (XVII) can be formally regarded as a product of the recombination of $C_6H_5-\dot{C}=O$ with the mesomeric cyclopropyl radical, but, in view of the stereospecificity of the process, the concerted mechanism involving the dissociation of compound (XVI) and the formation of a new bond must be regarded as more likely:

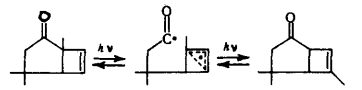


(XVI) (R = C_6H_5) (XVII)

b. Rearrangement of $\beta\gamma$-Unsaturated Cyclic Ketones

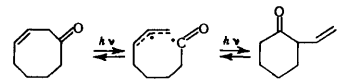
The allyl rearrangements of $\beta\gamma$-unsaturated cyclic ketones can take place with retention of the original number of carbon atoms in the ring (the position of the double bond or of substituents is altered) and with ring contraction or expansion. A characteristic feature of allyl rearrangements is their reversibility, i.e. the ratio of the isomeric ketones is independent of the isomer employed as the initial compound.

In 1960 Büchi and Burgess[207] described the rearrangement of a bicyclic $\beta\gamma$-unsaturated ketone, the mechanism of which can be represented as follows[208,209]:



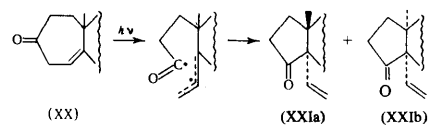
Subsequently a similar isomerisation was observed for other $\beta\gamma$-unsaturated bicyclic[208-210] and tricyclic[211] ketones.

One of the most typical examples of a rearrangement with a change in the number of carbon atoms in the ring is the conversion of cyclo-oct-3-en-1-one into 2-vinylcyclohexanone[212,213]:



(XVIII) (XIX)

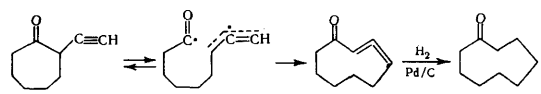
The ratio of compounds (XVIII) and (XIX) under the conditions of photoequilibrium is 7 : 40.[213] Ultraviolet irradiation of cyclodec-3-enone leads to a mixture of 2-vinylcyclo-octanone and the initial ketone in proportions of 2 : 5.[214] Similarly 2-isobutenylcyclopentanone was obtained from 2,2-dimethylcyclohepten-3-one[215]. A mixture of *cis*- and *trans*-isomers (XXI, a and b) was formed in the photolysis of the ketosteroid (XX), which is evidence of the intermediate formation of an acyl alkyl biradical[216]:



(XX) (XXIa) (XXIb)

Examples of the isomerisation of bicyclic ketones containing five-membered[217,218] and six-membered[210] rings to ketones with four-membered rings have been described.

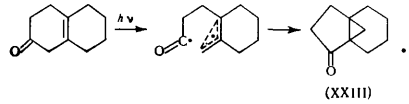
Acetylene—allene rearrangement. Carlson and Henton[219] described an interesting rearrangement of 2-ethnylcycloheptanone to a cyclic allene:



(XXII)

Compound (XXII) could not be isolated in a pure state, but its reduction gave a high yield of cyclononanone.

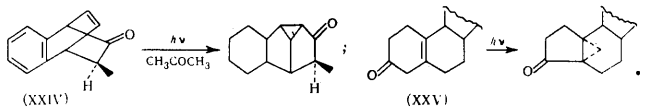
Rearrangements with formation and opening of rings are photochemical processes in which cyclopropane rings are mainly formed or cleaved. Ultraviolet irradiation of a solution of 2-oxo-1,2,3,4,5,6,7,8-octahydronaphthalene in t-butyl alcohol[220,221] gives the tricyclic ketone (XIII) in 60% yield:



(XXIII)

Cyclopropane hydrocarbons are obtained by the photolysis of six-membered $\beta\gamma$-unsaturated ketones only[220,221-224]. The solvent has a significant influence on the mode of photolysis. For example, when the ketone (XXIV)

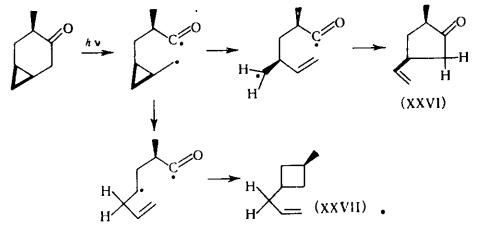
was irradiated in acetone, an isomeric ketone was obtained in 70% yield. In cyclohexanone solution only keten and naphthalene were obtained from compound (XXIV) [223]:



(XXIV) (XXV)

The photolysis of the $\beta\gamma$-unsaturated 3-oxosteroid (XXV), like that of compound (XXIV), is stereospecific and irreversible [221,222]. This is probably evidence that the dissociation of the C–C bond and the migration of the acyl group take place synchronously—a hypothesis which is consistent with conformation (XXV).

Irradiation of (–)-*cis*-4-caranone gives rise to C,C-migration of the acyl group and the opening of the cyclopropane ring [225]:

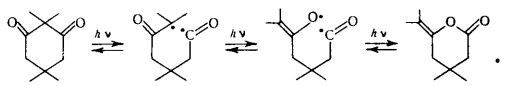


(XXVI) (XXVII)

The reaction is irreversible with (XXVI) : (XXVII) ≃ 3 : 1.

2. C,O-MIGRATION

Photolysis of compound (XXVIII) leads to the establishment in the solution of a photoequilibrium between compounds (XXVIII) and (XXIX) [229] with (XXIX) : (XXVIII) = 92 : 3.6:

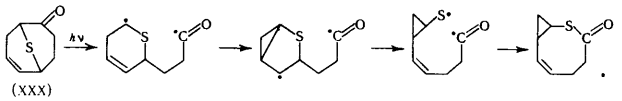


(XXVIII) (XXIX)

The rearrangement of other cyclic ketones containing two [227] or three [228] carbonyl groups in the β-positions relative to one another takes place similarly.

3. C,S-MIGRATION

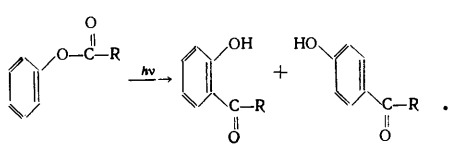
The recently described rearrangement of the thiaketone (XXX) belongs to this type of photochemical reactions [229]. One of the most likely mechanisms is



(XXX)

4. O,C-MIGRATION

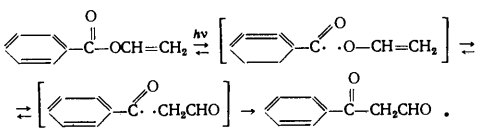
O,C-Migration of acyl groups has been observed in the photolysis of esters. The Fries photochemical rearrangement is best known:



Kobsa [230] proposed a free-radical mechanism for this reaction, according to which the bond between the carbonyl group and the ester oxygen atom is dissociated initially. The radical mechanism of the photochemical rearrangement of aryl esters has been fairly widely adopted, mainly because the reaction mixture always contains a phenol together with alkyl hydroxyphenyl ketones.

However, it has recently been shown [231] that the quantum yield of ketones is independent of the solvent, while the yield of the phenol decreases sharply as the viscosity of the medium increases. Consequently the formation of ketones takes place preferentially via a molecular mechanism and that of phenols via a free-radical mechanism.

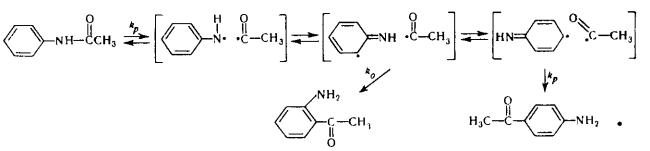
Ultraviolet irradiation of vinyl benzoate initiates the rearrangement according to the following probable mechanism [232]:



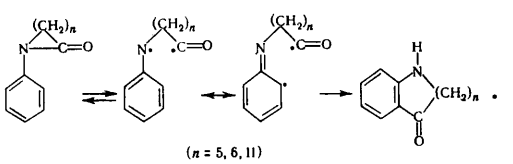
The intermediate formation of benzoyl radicals is also postulated in the photolysis of 1-cyclohexenyl benzoates [233].

5. N,C-MIGRATION

On ultraviolet irradiation, *N*-acylanilides isomerise in a manner similar to the rearrangement of aryl esters described above, with formation of a mixture of *o*- and *p*-acetanilides [234]. Shizuka [235] proposed a radical mechanism for this reaction:



The ratios of the rate constants for the recombination of the radicals $k_N : k_o : k_p = 1 : 0.35 : 0.6$ were calculated on the basis of the quantum yields of *o*- and *p*-acetanilides. The ratios are satisfactorily correlated with the "additional" π-electron density at the nitrogen atom and the carbon atoms of the benzene ring in the *o*- and *p*-positions: $\rho_N : \rho_o : \rho_p = 1 : 0.46 : 0.66$ (calculated ratios). The presence of an alkyl substituent at the nitrogen atom in acetanilide does not prevent the migration of the acyl group to the ring [236]. Consideration of the Fischer reaction [236] led to the development of a preparative synthesis of macrocyclic heterocycles:



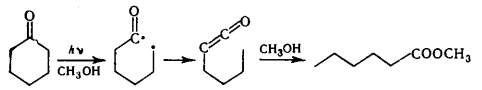
(n = 5, 6, 11)

VI. PHOTO-INITIATED DISPROPORTIONATION REACTIONS

1. REACTIONS WITH FORMATION OF UNSATURATED ALDEHYDES AND KETENS

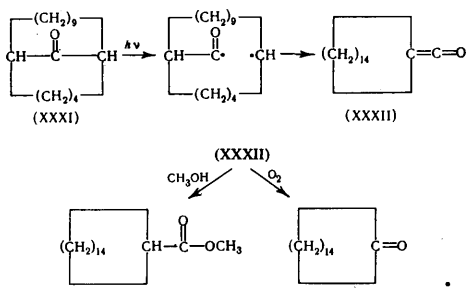
Many examples of the formation of unsaturated aldehydes in the photolysis of ketones in solution involving free radicals disproportionating in a solvent cage (Section II) are known. The reaction has been thoroughly described in monographs [29,34,35] and therefore will not be considered in detail in the present review.

The disproportionation of acylalkyl biradicals generated in the photolysis of cyclic ketones can result in the formation of a keten in addition to the unsaturated aldehyde. If the reaction is performed in the presence of water, an alcohol, or an amine, the keten is converted into an acid, an ester, or an amide [48,237]. For example, the main product of the photolysis of cyclohexanone in methanol is methyl caproate [237]:



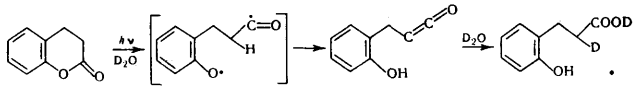
In contrast to cyclohexanone, in the photolysis of an alcoholic solution of cyclopentanone [237] only an insignificant amount of methyl valerate is obtained: in this case the second type of disproportionation of the acylalkyl biradical, leading to an unsaturated aldehyde, plays the main role.

Ketens are also formed when polycyclic ketones are irradiated with ultraviolet light [48,49,194,238-241]. Depending on the conditions, macrocyclic esters or ketones can be synthesised from bicyclic ketones of type (XXXI):



An ester is formed when the reaction is carried out in a carbon tetrachloride–methanol mixture and ketones are formed in carbon tetrachloride in the presence of oxygen [241].

An interesting rearrangement with ring opening was observed [231] when a cyclic lactone was irradiated in an aqueous dioxan solution:

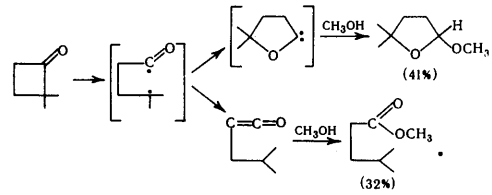


The intermediate formation of a keten was established by an isotope method [231-252].

2. REACTIONS WITH FORMATION OF OXACARBENES

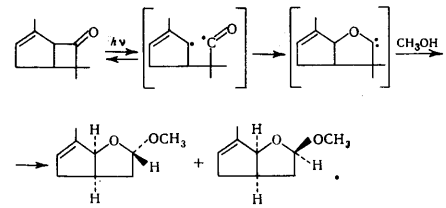
In a number of studies published in recent years [237,243-252] a new type of photochemical decomposition of cyclic ketones via a stage involving the generation of α-oxacarbenes was reported. The reaction takes place as a rule in the photolysis of alcoholic solutions of strained cyclic ketones [237]:

cyclobutanones [244,245,248,250], cyclobutanediones [246,247], camphor [252], and cyclocamphanone [243].



The photochemical reaction of *o*-phthalaldehyde probably also involves a carbene [251]. An oxacarbene is readily formed in the photolysis of aliphatic [249] and six-membered cyclic silaketones [237] in which the silicon atom is linked to the carbonyl group.

The involvement of acylalkyl biradicals in the formation of the oxacarbene was proved by Erman [253] by analysing the products of the photolysis of a bicyclic ketone:

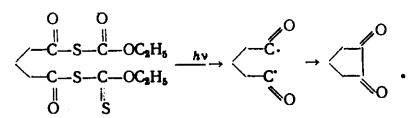


Identification in the reaction product of two epimeric bicyclic acetals is evidence that the dissociation of the carbon–carbon bond adjoining the carbonyl group precedes the formation of the oxacarbene.

Examples are known in which photolysis reactions of ketones involving a carbene take place stereospecifically [244,248,249]. In such cases the C–C bond probably dissociates via a concerted mechanism with formation of a carbene.

VII. OTHER REACTIONS

Acyl radicals are capable of dimerising to α-diketones. This reaction has been observed on ultraviolet irradiation of acetaldehyde [1], propionaldehyde [254], and isovaleraldehyde [254], on oxidation of acetaldehyde with oxygen [255] and manganese triacetate [27], on reaction of perfluoroacyl chlorides with nickel carbonyl [66], and on radiolysis of acetone [42]. An interesting example of an intramolecular recombination of acyl radicals as a result of the photochemical decomposition of a *cis*-*S*-acyl xanthate has been described [58]:



In the presence of hydrogen donors acyl radicals are converted into aldehydes [54,63,65].

When acyl radicals react with sulphuryl chloride [10-12,256], t-butyl hypochlorite [6-8], α-acyl-n-alkyl hypochlorites [74], carbon tetrachloride [16,63,69,173], bromotrichloromethane [13,14], and *N*-bromosuccinimide [14], they abstract a halogen atom forming acid halides. The preparation of acyl halides

from aldehydes using the above halogenating agents has a chain mechanism:

$$\left.\begin{matrix}\mathrm{RCHO}\\ \mathrm{XCl}\end{matrix}\right\} \xrightarrow[\text{(peroxide)}]{\Delta} \mathrm{R{-}\dot{C}{=}O} + \mathrm{X},$$

$$\mathrm{RCHO} + \mathrm{X}\cdot \rightarrow \mathrm{R{-}\dot{C}{=}O} + \mathrm{HX},$$

$$\mathrm{R{-}\dot{C}{=}O} + \mathrm{XCl} \rightarrow \mathrm{RCOCl} + \mathrm{X},$$

where $X\cdot = t\text{-}BuO\cdot$, $\cdot SO_2Cl$, $\cdot CCl_3$, etc.

Acyl radicals readily combine with oxygen and become converted into peroxy-radicals [257]:

$$\mathrm{R{-}\dot{C}{=}O} + \mathrm{O_2} \rightarrow \mathrm{R{-}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}{-}OO}\cdot$$

This reaction constitutes the basis of the industrial syntheses of acetic acid and acetic anhydride by the oxidation of acetaldehyde [255].

When di-t-butyl peroxide is decomposed in alcoholic or phenolic solutions of aldehydes in the presence of catalytic amounts (about 10^{-3} M) of variable-valence metal salts (Cu, Co, Fe, Mn), alkyl or phenyl benzoates are formed [258]. The formation of esters results from the one-electron oxidation of acyl radicals by the catalyst in the oxide form:

$$(\mathrm{CH_3})_3\mathrm{COC}(\mathrm{CH_3})_3 + \mathrm{Cu^I} \rightarrow (\mathrm{CH_3})_3\mathrm{COCu^{II}} + (\mathrm{CH_3})_3\mathrm{C{-}O},$$

$$(\mathrm{CH_3})_3\mathrm{C{-}O}\cdot + \mathrm{RCHO} \rightarrow (\mathrm{CH_3})_3\mathrm{COH} + \mathrm{R{-}\dot{C}{=}O},$$

$$(\mathrm{CH_3})_3\mathrm{COCu^{II}} + \mathrm{R'OH} \rightleftarrows \mathrm{R'OCu^{II}} + (\mathrm{CH_3})_3\mathrm{COH},$$

$$\mathrm{R{-}\dot{C}{=}O} + \mathrm{Cu^{II}OR'} \rightarrow \mathrm{RCOOR'} + \mathrm{Cu^I}.$$

Acyl radicals give up an electron most readily in reactions with copper(II) and cobalt(III) salts.

Decomposition of aqueous hydrogen peroxide in the presence of carbon monoxide, iron salts, and various organic compounds leads to the formation of carboxylic acids [70]. It has been suggested that [70] the intermediate acyl radicals are converted in this process into acylium cations [70].

The oxidation of $CH_3{-}\dot{C}{=}O$ with electron transfer is postulated as one of the stages in the decarboxylation of pyruvic acid by manganese(III) [259] and cobalt(III) [260] ions.

One-electron oxidation of acyl radicals probably occurs also in the following processes catalysed by copper salts: decomposition of t-butyl perbenzoate in aldehydes [261,262], photolysis of diacetyl [263,264], radiolysis of acetone [265], and oxidation of aldehydes by Fenton's reagent [266].

Thus, owing to the simplicity of their preparation and the wide variety of their chemical properties, acyl radicals are finding increasing application in organic chemistry.

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Structural Analysis of Natural Triglycerides

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An account is given of modern views on the structural analysis of triglycerides of natural fats by transesterification, lipase hydrolysis, determination of stereoisomerism, and establishment of polymorphism in their crystals. The possibilities of the practical application of these methods in fat analysis are shown. A list of 172 references is included.

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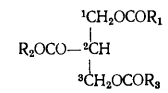
I. INTRODUCTION

It was assumed for a long time that natural fats were mixtures of simple monacid triglycerides (I) in which the alkyl groups R were identical ($R_{(1)} = R_{(2)} = R_{(3)}$).



(I)

At the beginning of the twentieth century, however, mixed-acid triglycerides based on (I: $R_{(1)} \neq R_{(2)} \neq R_{(3)}$, $R_{(1)} \neq R_{(3)}$) were isolated from several fats. The problem of the structure of triglycerides arose. The hypothesis of a statistical distribution of acyl residues RCO in triglycerides, according to which the probability of formation of a particular individual triglyceride was determined solely by the molar concentration of its component fatty acids in the given fat and by the frequency of occurrence of these acids in the given triglyceride was soon abandoned, and the search for the laws governing the glyceride structure of natural fats has continued to the present time.

The present Review makes a systematic survey of the development of work on the positional distribution of acyl groups in triglycerides—from the original discovery by transesterification of the non-statistical character of the structure of natural fats to the establishment by lipase hydrolysis of the non-equivalence of the 1,3- and the 2-positions in the glycerides, and finally to the recent discovery of the stereospecificity of the structure of animal and plant triglycerides. The last section of the Review deals with the polymorphism of glycerides, which, in combination with their chemical synthesis (Section II, 3), is also used to establish the structure of individual triglycerides in natural fats.

II. ESTABLISHMENT BY TRANSESTERIFICATION OF THE NON-STATISTICAL DISTRIBUTION OF ACYL RESIDUES IN NATURAL TRIGLYCERIDES

1. Transesterification of Triglycerides

Transesterification is the free redistribution (randomisation) of acyl groups among glycerides under the influence of certain physical and chemical factors, as a consequence of which the structure of the glycerides becomes statistical instead of oriented. It is the oldest method in the structural chemistry of natural triglycerides, for the discovery of marked changes in melting point and other properties of fats after randomisation was the immediate reason for posing the problem of their structure. During actual transesterification the initial and final products are triglycerides: depending on whether the acyls migrate within a single glyceride or between different triglycerides, we can distinguish intramolecular and intermolecular transesterification. Glycerolysis—the transesterification of a fat with excess of glycerol—results in the appearance of a large quantity of mono- and di-glycerides. Transesterification is of great practical as well as theoretical value: the changes in polymorphism, melting point, texture, plastic range, and other properties of a fat accompanying randomisation and glycerolysis greatly influence its digestibility and its suitability for the manufacture of margarines, monoglyceride emulsifiers, and other technical products having specified properties [1-6].

Transesterification can be accomplished [6-31] by treating a fat free from moisture, free acids, and peroxides in several ways—(1) in the absence of a catalyst at 300°C, (2) with alkaline catalysts at 100–140°C with 0.03–0.3% of sodium methoxide, at 30°C with 0.6% of sodium methoxide for 1 h (for a 3 : 2 mixture of an oil and hexane), or at 20°C with 0.005% of lithium t-butoxide for 12–15 h (for a 1 : 10 mixture of a fat and dimethylformamide), (3) with naphthalene-2-sulphonic acid as catalyst, or (4) with tin and its salts or dihydroxide at 225°C [2,3,6,9,10]—after which the catalyst is neutralised, and the glycerides are purified [11]. The most effective catalyst is sodium methoxide, but at high temperatures complete randomisation of the composition cannot be obtained, though under milder conditions a purely statistical mixture of glycerides is produced [13]. A statistical mixture of triglycerides can also be obtained by transesterification of the methyl esters of fatty acids with triacetin (Ac_3), [8] but the transesterification of cocoa-butter with ^{14}C-tristearin and tritium palmitate yields uniformly labelled ^{14}C- and ^{3}H-triglycerides [12]. Lagrange's rule of multipliers for a system of any two fatty acids A and B shows that the maximum content [A_2B] of a glyceride A_2B is reached when [A] = 2[B]; we then have the contents 44.4%, 29.7%, 22.2%, and 3.7% for [A_2B], [A_3], [AB_2], and [B_3] respectively. These calculations are used in selecting the acid concentrations for the preparation of a mixture of glycerides of a specified composition [4,7].

As already mentioned, the properties, composition, and structure of triglycerides are greatly changed by transesterification. The changes in the Bömer number and in the melting point depend on departures from the random values in the concentrations in a given fat of glycerides containing only saturated acyls [Sat_3].[2] Appreciable changes occur also in the phase structure of the triglycerides (Section V, 3). When molten pork fat, containing 25% of 2-palmito-oleostearin (2-PalOlSt), is chilled rapidly, coarse crystals of the β'-3-polymorphous form of this glyceride are produced, and prevent the use of this fat in the confectionary industry. After transesterification the 2-PalOlSt content falls to the statistical value (3.4%), and readily fusible Sat_2Unsat glycerides of vegetable type appear; these crystallise in the β'-2-form, the granularity of the product disappears, and its emulsifying power improves [4,14]. It is possible also to change the properties of a fat in the required direction by controlled transesterification, in which the randomisation of liquid fats such as cottonseed oil is combined with low-temperature crystallisation, which removes saturated acids from the mixture as a Sat_3 precipitate [4,7].

The transesterification of natural and artificial fats usually increases the total number of individual triglycerides of differing polarity [15-18]. Olive oil yields the new glycerides OlPalLinoleoyl and OlStLinoleoyl, and a mixture of St_3 and Ol_3 is converted into the more complicated statistical mixture of StStSt, OlStSt, StOlSt, StOlOl, OlStOl, and OlOlOl [11,19]. The structure of transesterified fats is usually close to the statistical structure, independently of the presence of a solvent in the reaction mixture.

However, selective physicochemical reaction parameters (preferential re-esterification of acids having a longer chain, differences in reactivity between 1- and 2-hydroxy-groups of glycerol, etc.) often divert the distribution of acyls in the randomised oil from the calculated distribution [2,19,21]. Such deviations have been found, in particular, in the composition of transesterified fats rich in volatile acids, such as coconut oil and especially randomised milk fat, which differs appreciably from the original fat (Fig. 1A) in its content of triglycerides in which the total number of carbon atoms in all the acyls is $m = 50-54$) (Fig. 1B) [13,19]. The equilibrium mixtures obtained by transesterifying St_3, Ol_3, and Ela_3 (where Ela = elaidate) or a mixture of the methyl esters of the fatty acids with Ac_3, have the statistical composition [8,17,22]. The content of fractions of different polarity does not vary so greatly in the transesterification of liquid oils (safflower and olive) as in the randomisation of solid cocoa butter [12, 18,21]. The transesterification of sunflower and cottonseed oils produced statistical distributions of unsaturated acyls in individual groups of triglycerides [23]. The composition of milk fat, pork fat, soya-bean oil, and olive oil after transesterification corresponded to the statistical distribution [10,15]. If the content of saturated acyls at position 2 of the glycerides [$Sat_{(2)}$] is lower after randomisation of a vegetable oil, contamination of the oil with fats obtained by esterification is indicated [20].

2. Glycerolysis of Triglycerides

A fat is subjected to glycerolysis by heating it with excess of glycerol in 0.1% caustic soda in a stream of an inert gas. Cessation of reaction and the establishment

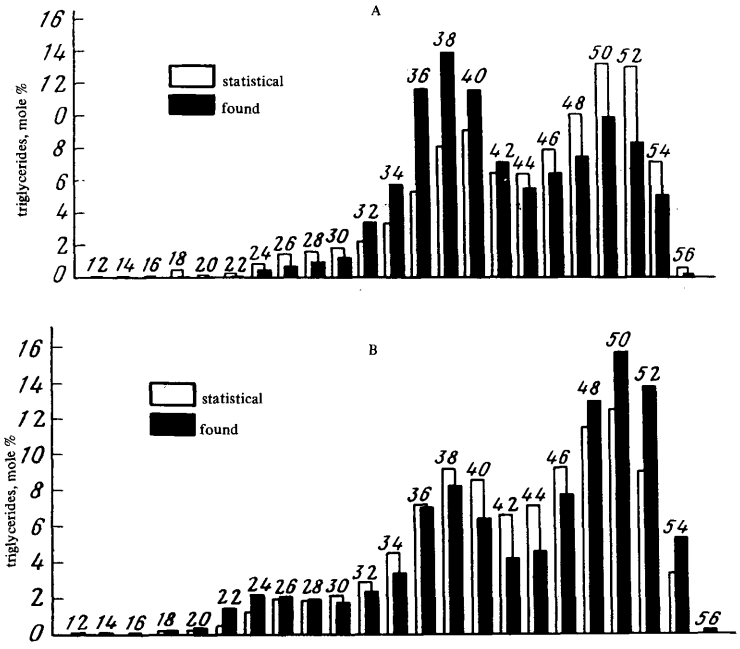


Figure 1. Composition of triglycerides of milk fat [13]: A) native; B) transesterified. The numerals 12-56 indicate the numbers of carbon atoms in individual fractions.

of dynamic equilibrium are assessed from the solubility of the mixture in 2–5 parts of methanol. The equilibrium constant K_e of glycerolysis is calculated from the contents in the mixture of glycerol, 1(3)- and 2-monoglycerides, 1,3- and 1,2(2,3)-diglycerides, and triglycerides determined by adsorption chromatography, measurement of the hydroxyl, acid, and saponification numbers, and also periodate oxidation [16,24]. Such calculation established a fundamental fact in triglyceride chemistry: positions 1 and 2 are not equivalent with respect to acylation [25–29].

Table 1. Composition (wt. %) of equilibrium mixture of glycerolysis* products [24].

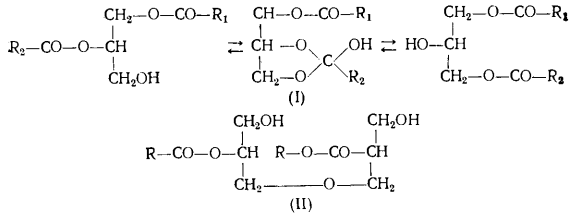
Components	Found	Calculated for	
		$K_e=3.4$	$K_e=1$
Glycerol	6.5	6.5	6.5
1(3)-Monoglycerides	36.5	39.5	28.3
2-Monoglycerides	4.4	5.1	14.2
1,2(2,3)-Diglycerides	15.6	14.1	27.0
1,3-Diglycerides	32.7	26.9	13.5
Triglycerides	4.3	7.9	10.5

*Linseed oil (1 mole) and glycerol (1.85 mole) were heated with 0.1% trisodium orthophosphate at 240°C for 2 h.

If glycerolysis occurred strictly quantitatively, and the probability of esterification was the same for glycerol derivatives containing free primary and secondary hydroxy-groups (R^POH and R^SOH), the molar contents of esterified (a) and free (b) hydroxyl in the mixture could have been used to calculate the statistical concentrations of tri-, di-, and mono-glycerides and of free glycerol as ($\times 10^{-4}$) respectively a^3, $3a^2b$, $3ab^2$, and b^3. [4,26] In this case the relative molar concentrations of positional isomers in the monoglycerides and diglycerides at the equilibrium $R^POH + R^SOOCR \rightleftharpoons R^SOH + R^POOCR$ would have been [1(3)-MGl] = 2[2-MGl] and [1,2(2,3)-DGl] = 2[1,3-DGl], while the equations K_e = [1(3)-MGl]/2[2-MGl] = [1,2(2,3)-DGl]/2[1,3-DGl] would give a calculated value of $K_e = 1$. However, the equilibrium concentrations obtained by the usual glycerolysis (at 175–180°C) were [1(3)-MGl]/[2-MGl] = 88 : 12 and [1,2(2,3)-DGl]/[1,3-DGl] = 40–60, from which $K_e = 3.0 \pm 0.6$. Hence the free energy of a primary hydroxy-group of glycerol on esterification $\Delta F = -RT \ln K_e$ exceeds the free energy of the secondary group by 1.2 kcal mole^{-1}, and the probability of esterification of a primary hydroxyl is treble that of the secondary group [26,27]. The composition of the equilibrium mixture calculated with $K_e = 3.4$ agrees well with the experimental results, but those calculated with $K_e = 1$ show marked discrepancies (Table 1) [24]. Increase in the number of carbon atoms m and decrease in the number of double bonds e in the acyl residue diminishes the rate of acyl migration, but does not affect the value of K_e. [25] Substitution of one primary hydroxyl does not affect the rate of esterification of the other primary group. With fall in the temperature of the reaction K_e increases [28].

Little work has yet been done on the mechanism of transesterification and glycerolysis [30–32]. Transesterification itself may be a particular case of glycerolysis, in which, under the influence of the catalyst and of the free hydroxyls of water as initiators of the reaction, traces of glycerol, monoglycerides, and diglycerides continually appear in and disappear from the mixture, with a consequent dynamic equilibrium (randomisation) of the acid radicals [4]. A cyclic orthoester (I, Scheme 1) may be an intermediate product in the acyl migration [31].

Scheme 1



Study of the migration of the acyl groups in mono- and di-glycerides in ethereal hydrogen-chloride solution has shown that this reaction requires the presence of traces of water. The mixture formed by the transesterification of a 2-monoglyceride contains a 1,7-dihydroxy-4-oxa-heptane-2,6-diyl dicarboxylate (II) (a dimerised ether), and corresponding derivatives are formed by the transesterification of 1(3)-monoglycerides and 1,3-diglycerides. According to one view an equilibrium mixture of the 2-monoglyceride and (II) is produced in the solution, after which rupture of the ether bond occurs with simultaneous intramolecular migration of the acyl group and formation of a 1(3)-monoglyceride [30]. According to another author (II) is not an intermediate but a secondary product of the reaction, which is synthesised by the combination of a monoglyceride or a diglyceride with the corresponding acid chlorides formed by the action of hydrogen chloride on these glycerides [32].

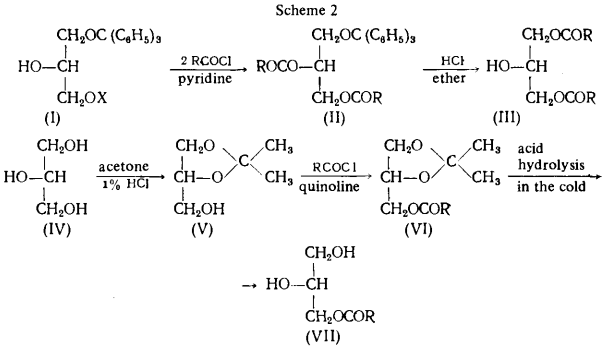
3. Chemical Preparation of Triglycerides of Definite Structure

Together with transesterification, the preparation of specified triglycerides (of a mixture of stereoisomers—see Section IV, 8) for comparison with natural triglycerides (melting point, polymorphism, etc.), in order to identify the latter, was one of the earliest methods of investigating fats [33–37]. Monacid triglycerides (AAA) are prepared by the single-stage direct esterification of excess of the fatty acid with glycerol in the presence of toluene-p-sulphonic acid. The preparation of diacid and triacid triglycerides is a multistage process with protection of particular hydroxy-groups at individual stages, and also the isolation, purification, and identification of intermediate products [5,34].

Symmetrical triglycerides ABA are obtained by combining 1,3-diglycerides of acid A, which are easily segregated from the more easily fusible 1,2(2,3)-diglycerides by crystallising the equilibrium mixture, with excess of the chloride of acid B by heating in chloroform–pyridine solution [36]. Migration of acyl groups, which is very considerable when toluene-p-sulphonic acid is used as catalyst, is absent from this reaction. A statistical mixture of the 1,3-diglycerides of palmitic and stearic acids on reaction with oleoyl chloride gave a mixture of triglycerides similar to cocoa butter [12].

Scheme 2 shows the reactions involved in the preparation of 1,3-diglycerides of polyunsaturated acids (I–III) and 1(3)-monoglycerides (IV–VII). 1,3-Diglycerides of polyunsaturated acids (III) which crystallise with difficulty are prepared by acylating the 1(3)-monotrityl ether of glycerol (I: X = H) and then detritylating with quantitative migration of the 2-acyl to the outer position. Unsymmetrical diacid triglycerides AAB are obtained by using the chloride of acid A to acylate 1(3)-monoglycerides of acid B (VII: R = B), prepared by Fischer's method with 1,2(2,3)-isopropylidene protection subsequently removed by acid hydrolysis [29,38].

Scheme 2



Finally, the preparation of a triacid triglyceride (ABC) involves first obtaining the 1(3)-monoglyceride of acid A (VII: R = A) by the mechanism (IV) → (VII), and then converting it into the 3(1)-monotrityl ether (I: X = COA), which is esterified in the 2-position by the chloride of acid C with subsequent acyl migration by the mechanism (I) → (III) to give the 1,3-diglyceride of acids A and C (III: R = A or C); this is substituted at position 2 by the chloride of acid B. If C is an unsaturated acid, the trityl protection in (II) is removed by hydrogenolysis without acyl migration, and the resulting 1,2(2,3)-diglyceride is acylated at the last stage by the chloride of another unsaturated acid to form a triacid triglyceride of type $SatUnsat_2$. [4,35]

III. STRUCTURAL ANALYSIS OF TRIGLYCERIDES BY LIPASE HYDROLYSIS

1. Lipase Hydrolysis of Triglycerides

It was discovered as early as 1945 that the lipase hydrolysis of fats in the intestine ceased long before all the ester bonds had been cleaved [1,35,39–45]. Subsequent experiments with synthetic triglycerides of known structure showed that 1,2(2,3)-isomers predominated among the diglycerides present in the products of incomplete hydrolysis [39,44]. The preferential detachment by pancreas lipase *in vivo* and *in vitro* of the outer acyls in triglycerides of saturated and unsaturated acids having $m = 12–18$ is indicated also by the incorporation of ^{14}C-labelled free fatty acids, in the presence of lipase and a fat, only in the 1,3-positions of triglycerides, and by the formation of the 2-isomers of monoglycerides on lipase hydrolysis, as demonstrated by their isomerisation with perchloric acid and periodate oxidation [40 46–51]. On the basis of these discoveries a method was proposed in 1956 for determining the composition of acyl groups in the 1,3- and 2-positions of triglycerides in natural fats from the composition of the free fatty acids and of 2-monoglycerides resulting from its enzymic cleavage [48]. Lipase hydrolysis is now the principal method for the structural analysis of triglycerides [42,47].

In contrast to esterases, which hydrolyse water-soluble substrates, lipase (glycerol ester hydrolase, EC 3.1.1.3) is almost completely specific to 1,3-esters of glycerol which have limited solubility in water [52,55]. In oil of ergot, for example, it does not cleave the ester bonds between the ricinoleate residues and the glycerol [56]. Furthermore, lipase possesses no stereoselectivity (Section IV, 1). [39] The simplified lipase reaction can be divided into two stages:

$$\text{TGI} \xrightarrow{k_1} \text{1,2(2,3)-DGI} \xrightarrow{k_2} \text{2-MGI} \quad .$$

Each stage has its own rate constant: for the oil from *Madhuca longifolia* the constants are $k_1 = 0.35$ and $k_2 = 0.36$; but the corresponding values for pork fat are 0.31 and 0.36. From the equation for the reaction we find that (where e is the base of natural logarithms and t the time of reaction) [52]

$$[\text{TGI}]_t = [\text{TGI}]_0 \cdot e^{-k_1 t};$$

$$[\text{DGI}]_t = [\text{DGI}]_0 + [\text{TGI}]_0 \cdot [k_1/(k_2 - k_1)]\,(e^{-k_1 t} - e^{-k_2 t});$$

$$[\text{MGI}]_t = [\text{MGI}]_0 + [\text{TGI}]_0\{1 - [1/(k_2 - k_1)]\} \cdot (k_2 e^{-k_1 t} - k_1 e^{-k_2 t}) \quad .$$

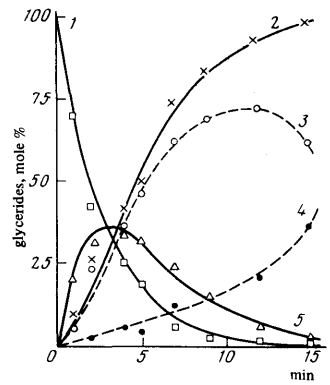


Figure 2. Dependence of lipase hydrolysis of oil of the plant Madhuca longifolia on time of reaction [52]: 1) triglycerides; 2) monoglycerides + glycerol; 3) monoglycerides; 4) glycerol; 5) diglycerides. The full curves represent calculated concentrations (Section III, 1), and the broken curves the experimental values.

Before hydrolysis the protein of the enzyme is absorbed on the surface of the fat micelles, and therefore the reaction velocity depends on the degree of emulsification of the substrate in the aqueous solution, which determines the area of this surface, and also on the relative quantities of enzyme and fat [57]. The free fatty acids and monoglycerides formed by hydrolysis are desorbed into the aqueous phase [55]. The rate of the reaction gradually decreases, since triglycerides, 1,2(2,3)-diglycerides, and

2-monoglycerides release 2, 1, and 0 mole respectively of acids per mole of glycerol [53]. Maximum contents of diglycerides and monoglycerides are observed after 40% and 70% hydrolysis respectively (Fig. 2). Free glycerol may appear in the medium after 25–40% hydrolysis, as a consequence of acyl migration (Section III, 3) [47,52]. Several reviews have been published on the properties, kinetics, and mechanism of the reaction of pancreatic lipase [1,41,43,44,54].

Table 2. Reaction conditions (per 1 g of fat) in studying the structure of triglycerides by lipase hydrolysis (data in parentheses relate to the micromodification of the method) [1,10,35,47,55,56,58–64].

Parameter of reaction medium and units of measurement	Numerical value
Composition and concentration of buffer solution	1.2 M or 1 M NH_4OH-NH_4Cl
Quantity of buffer solution	18–23 (160–1050)
Optimum pH of buffer solution	8.0–8.5
Sodium taurocholate, mg	5–20 (250–500)
Calcium chloride, mg	350–440 (2000–8000)
Enzyme, mg	70–400
Temperature of medium, °C	37–40
Duration of incubation, min	10–90 (2–30)
Degree of hydrolysis of ester bonds, %	50–70
pH of medium after addition of 1–6 *N* HCl	1–3
Atmosphere	nitrogen or air
Rate of stirring of mixture, rev/min	120–3000

2. Conditions of Lipase Hydrolysis

The conditions under which lipase hydrolysis is conducted are summarised in Table 2. The source of the enzyme is usually the secretion or a preparation of pig pancreas—pancreatin, steapsin, etc.—which may vary greatly in activity and in positional specificity [15,42,56,59]. The quantity of lipase is chosen to give a 65–70% yield on hydrolysis for the minimum time, and its specificity is checked by its action on synthetic triglycerides of known structure [44,47,49,58,64]. The activity of the enzyme increases by a factor of 135 on purification, which includes removal of fat, extraction with water, adsorption on aluminium hydroxide, precipitation with ammonium sulphate, dialysis, and chromatography on DEAE cellulose. However, purification does not improve positional specificity, and for the study of glycerides, therefore, it is usually restricted to Desnuelle's stage (II). [40,43,65,66] It is important to remove endogenous lipids from the preparation, and to eliminate any esterase activity (if glycerides of acids having $m < 12$ are under investigation) and non-specific "lipase" activity, which sometimes amounts to 2–10% of the total lipase activity, is promoted by a taurocholate, and is inhibited after 2 h at pH 9 and 40°C. [62,63,67,68]

The substrate—natural or synthetic triglycerides—and other reactants are also freed from any contamination with mono- and di-glycerides [44,69]. Unsaturated glycerides are hydrolysed in an atmosphere of nitrogen (Table 2). Only a liquid and well emulsified substrate undergoes cleavage [15–39], and therefore the mixture with the emulsifier is homogenised by heating before addition of the lipase. As acyl migration and inactivation of the enzyme increase above 40°C, homogeneity of the medium is best created by rapid mechanical stirring [40,43,47]. The usual emulsifier is sodium taurocholate, which, however, activates the foreign "lipase" (see above) and exerts a still not altogether clear promoting effect on the pancreatic lipase itself [41,59]; polymers—polyvinyl alcohol, gum arabic, etc.—are also used [42,61]. However, the emulsifiers are often inadequate for the production of good emulsions from solid Sat_3 glycerides (chain length of each acyl $m_S > 12$); in that case they are mixed, before emulsification, with liquid carrier lipids, which do not influence the specificity of hydrolysis of saturated substrates [70,71]. Mixing an Sat_3 glyceride with triolein (1 : 1 or 4 : 1) contaminated the reaction mixture with hydrolysis products of the latter, and therefore it is now replaced by methyl esters—methyl oleate, methyl pentadecanoate, etc. [55,63,69]

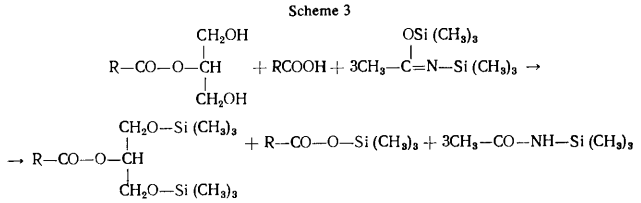
With hydrolysis on a macro-scale, when the molar ratio of fat (0.2–2 g) to buffer is ~ 1.5, the pH falls rapidly below the optimum value (Table 2). [10,47,59,61,63] To avoid inactivation of the lipase the optimum pH must be maintained by adding ammonium hydroxide or 0.5–1 *N* caustic soda either manually or by means of a recording pH-stat, which enables the point of maximum content of monoglycerides in the medium to be detected (Fig. 2). [42,56,59,63,72] In the micro-method (1–50 mg of fat) the existing buffer solution usually ensures maintenance of the optimum pH [47,65]. Calcium ions (Table 2) bind free fatty acids, and therefore hydrolysis proceeds to the monoglycerides; in the absence of the calcium ion, or in the presence of a phosphate buffer to combine with it, only diglycerides are produced, and free fatty acids accumulate and inactivate the enzyme [43,44,55]. If time t elapses between addition of the lipase and the appearance of turbidity due to insoluble calcium salts, time $2t$ corresponds to the maximum content of monoglycerides [41,54]. Reaction is terminated by excess of hydrochloric acid, and the total lipids are extracted [40,57,61,73].

The structure of natural triglycerides is determined from the composition of the products of lipase hydrolysis. The composition of the mono- and di-glycerides can be established by gas chromatography of their acetates: monoglycerides could be separated as far as monoarachin, and diglycerides as far as palmitomyristin. Acetates of 1-monoglycerides and of 1,3-diglycerides were eluted more slowly than the derivatives of 2-monoglycerides and 1,2-diglycerides respectively [74]. A mixture of 1- and 2-monoglycerides was analysed by treatment with methanesulphonyl chloride and an acetone solution of sodium iodide: 2-monoglycerides pass into the 1-isomers, and the resulting allyl esters of fatty acids are separated on the non-polar liquid phase at 240°C for 60 min [75,76]. Quantitative determination of the hydrolysis products of glycerides containing acid-labile groups in the chain of the fatty-acid residues was accomplished by gas chromatography of the unchanged triglycerides and the trimethylsilyl derivatives of monoglycerides, diglycerides, and free aliphatic acids, which were obtained in a 20% solution of bistrimethylsilylacetamide in pyridine (Scheme 3). The trimethylsilyl ethers of monoglycerides and diglycerides and the trimethylsilyl esters of fatty acids were immediately separated by temperature programming. This method was used for the positional analysis of glycerides of *cis*-12,13-epoxyoleic, 10-hydroxyoctadeca-*trans*-9,*trans*-12-dienoic, and octadeca-*cis*-9,*trans*-11,*trans*-13-trienoic acids; decomposition products obtained by other methods of silylation were absent here [77].

The products of lipase hydrolysis—unchanged tri-, di-, and mono-glycerides, free fatty acids, and glycerol—are usually isolated by thin-layer or column adsorption chromatography [40,78–89]. If the adsorbent is impreg-

nated with boric acid, diglycerides and monoglycerides are separated into symmetrical 1,3- and 2-isomers and into unsymmetrical 1,2(2,3)- and 1(3)-isomers respectively [65,79]. Each class of lipids is considered quantitatively, and the composition of their acids is determined by gas chromatography [60,78,84,85]. From the content of a fatty acid in the original fat [A] and for one position in the triglycerides, the composition of another position is calculated by means of the formula $3[A] = 2[A_{(1,3)}] + [A]_{(2)}$, and the content of A in the 2-position is $H = 100[A_{(2)}]/3[A]$. [17, 44,80,82,90-92] Acyl migration (Section III, 3) is assessed by decomposition 1(3)-monoglycerides with periodate, and reisolating the 2-monoglycerides [64,83,87,90]. The structure of diglycerides and monoglycerides is determined also by esterifying them with chlorides of fatty acids not present in the given fat, subjecting the artificial triglycerides obtained to further lipase hydrolysis, and examining the cleavage products of the latter [46,68].

Scheme 3



3. Determination of Reliability of Enzymic Analysis of Triglycerides

In order to assess the reliability of the results of lipase hydrolysis it is necessary firstly to ascertain whether the rates of elimination of different fatty acids are the same and whether it is a random process, and secondly to know whether positional specificity of hydrolysis is maintained and how it is affected by possible migration of acyl groups [43,60,68,73,93-101].

No great changes in composition of the acids of each class of lipids (Section III, 2) were observed with different times of hydrolysis of ordinary fats having $[Sat_{(2)}] < 10\%$ and $m = 12-18$ carbon atoms in saturated and unsaturated acids; the unchanged triglycerides and combined fraction of free fatty acids and 2-monoglycerides were similar in acid composition to the original fat (provided that the diglyceride content of the mixture was low). Thus there is little fatty-acid specificity in the reaction, while the hydrolysis of 1,3-acyl groups is itself a random process [1, 40,44,52,57,71,99-107].

Acids having $m:e = 20:5$ and $22:6$ in the fats of marine animals, owing to the proximity of their carboxyls to the first double bond and the terminal methyl group (as a consequence of bending of the chain), are detached more slowly than ordinary acids by factors 5–10, and therefore accumulate in the diglycerides and triglycerides of the reaction mixture. The 22:5 acyls, which do not exhibit these steric features, are hydrolysed normally. Lipase hydrolysis has now been replaced by use of a Grignard reagent—methylmagnesium bromide—for the structural analysis of "marine" fats [80,95,107].

On the other hand, short-chain acyls ($m < 12$), owing to the ease of their migration from the 2-position to the 1,3-position in 2-monoglycerides and 1,2(2,3)-diglycerides, are hydrolysed at three times the rate for ordinary acids, so that they accumulate in the monoglycerides. Therefore the results of lipase hydrolysis for milk fat, the fat of Cuphea llavia, the oil of Irvingia gabonensis, and other fats rich in volatile acids are unreliable. The degree of migration of lauric acid, which occupies a position intermediate between volatile and non-volatile acids, has not yet been determined [16,39,53,82,87,93,94, 96,97,100,102-104,106].

Chain branching inhibits the detachment of acyl groups, but the introduction of a hydroxy-group has no effect on the rate of hydrolysis. The dibasic acyls in triglycerides containing azelaic acid were hydrolysed like ordinary acyl groups. Unsaturated acyl groups in pork fat ($[Sat_{(2)}] \simeq 75\%$) were eliminated preferentially, which increased the saturation of the remaining triglycerides and diglycerides. The composition of 2-monoglycerides $[Sat_{(2)}]$ remained unchanged, and therefore calculation of $[A_{(1,3)}]$ (Section III, 2) and the structure of glycerides from $[A_{(2)}]$ and [A] is more correct than the previous calculation of $[A_{(2)}]$ from the variable composition of free fatty acids. Results for the effect of *cis–trans* isomerism on the rate of hydrolysis are contradictory [41,46,47,54,59,98,105].

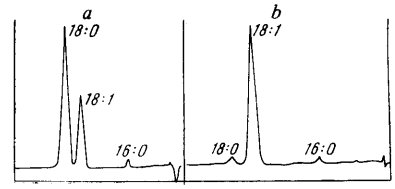


Figure 3. Gas–liquid chromatograms of fatty acids: *a*) 1,3-distearo-2-olein; *b*) 2-monoglycerides obtained by lipase hydrolysis of (*a*) [55].

The hydrolysis of synthetic and natural glycerides in the intestine and on a micro-scale *in vitro* for 1–2 min (Fig. 3) corresponds to the chemical equation (Section III, 1) [42,52,57,83]. With increase in the time of reaction the monoglycerides isomerise: they are usually found to contain 10–30% and more of 1(3)-monoglycerides formed by the migration of acyl groups in an aqueous medium at pH 8, and easily converted into glycerol (up to 30–40% by the end of the reaction) [39,66,71]. Isomerisation can be partly eliminated by adding free fatty acids or by using microbial lipases with an acid optimum pH (section III, 4) [41,49,108]. The migration of acyl groups is directed thermodynamically to the 1,3-positions, and its rate is lower than that of detachment. Therefore 2-monoglycerides are free from acyl groups present in the 1,3-positions of the initial triglycerides, and the composition of their acids corresponds to that of the 2-position of these triglycerides [46,47,82].

The positional specificity of lipase is almost absolute [44, 55,105]. Thus hydrolysis of the acylation products of 1(3)- and 2-monoglycerides (Section III, 2) resulted in the elimination of 98% and 2–10% respectively of the original acid, but the composition of the hydrolysis products from derivatives of 1,2(2,3)- and 1,3-diglycerides corresponded to the theoretical value within 5%. Similar results have been obtained in experiments with 1,3-benzylidene-2-oleoylglycerol and 1,3-dihexadecyl-2-oleoylglycerol, where migration of oleate is excluded, while foreign "lipase" (Section III, 2) is inhibited [62,68].

Quantitative estimate were made of migration and specificity of hydrolysis by subjecting 2-[9′,10′-$^3H_2$]oleoyl-1,3-dipalmitoyl-*sn*-glycerol to cleavage at the constant pH = 8 (Table 3 and Fig. 4). The acid composition of the reaction products diverged from the theoretical only as a consequence of the isomerisation of 1,2(2,3)-diglycerides and especially 2-monoglycerides, which increased during incubation; the content of 1-monoglycerides and free oleate in the hydrolysis products did not exceed 3–5%.

Table 3. Hydrolysis of 1,3-dipalmitoyl-2-[9′,10′-$^3H_2$]-oleoylglycerol by pancreatic lipase (mole %).[65]

Time, min	Free fatty acids in products	Content of ^3H (%) in				1,3-PalOl × 100 / 1,2-PalOl	Moles per 100 moles of 2-MGl		
		TGl	DGl	MGl	FFA		all 1-MGl	1-MOl	1-MPal
19	31	26	34	37	3	2	23	20	3
22	50	17	27	52	4	3	23	20	3
30	60	6	15	74	5	4	38	35	3
45	60	11	15	66	8	6	43	38	5

The radioactivity of the triglycerides, diglycerides, and monoglycerides obtained from the tritiated triglyceride by hydrolysis with the lipase of the mould Rhizopus arrhizus was respectively 60, 59.9, and 55.5 (in 10^3 d.p.m. μ mole^{-1}), which indicates slight migration of the tritiated oleoyl from the 2-position[65].

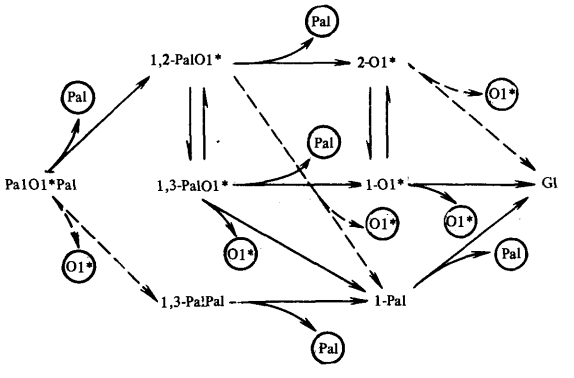


Figure 4. Possible transformations of PalTOlPal on lipase hydrolysis[65], Full lines represent normal hydrolysis of 1,3-acyl groups, and broken lines abnormal hydrolysis of 2-acyl groups. The symbol ⇌ denotes spontaneous acyl migration.

Lipase was used originally for the hydrolysis either of synthetic individual triglycerides or of natural fats of complicated glyceride composition[40,42,44,50]. The results were expressed as the acid composition at 2- and 1,3-positions. The calculation was also based on values of H (Section III, 2), other parameters of the positional distribution of individual acids, and the composition of the fat glycerides from the appropriate equations[64,68,93,105]. When $H \simeq 33\%$, a purely statistical distribution of the given acyl group is present[71,82,106]. However, this seldom occurs[63]: the structure of most animal and vegetable fats diverges greatly from the statistical[43,45,83]. The differences in composition between the 1,3- and 2-positions led to the hypothesis that two enzymes, differing in fatty-acid and positional specificity, were responsible for the synthesis of glycerides[35,49,73]. It has now been shown that the best method for the structural analysis of glycerides is a combination of a micromethod of lipase hydrolysis with preliminary chromatography of the fats[1,41,47,54,72,87].

The defects of lipase hydrolysis are the sometimes poor reproducibility of the effects of different lipase preparations containing various impurities, the migration of acyl groups, the re-esterification of free fatty acids due to the transferase activity of lipase on prolonged incubation in the absence of calcium ions, and the absence of stereospecificity of hydrolysis[1,39–42,47,54,67,109–111].

4. Use of Other Lipases for the Analysis of Triglycerides

Besides the pancreatic lipase of the pig, the corresponding enzymes from other mammals, and also the lipases of cod, skate, and lobster, which have the same positional specificity, are used in the analysis of fats[39,43,79,112–114]. Lipases of milk and of the fungus Pseudomonas fragi are also specific to the 1,3-positions. The optimum pH for their functioning is 5.6, and therefore acyl migration is less pronounced than with pancreatic lipases[1,44,100,115]. The lipase of Vernonia anthelmintica seeds attacks the 2-position to give 1,3-diglycerides. The enzyme of the fungus Geotrichum candidum is specific, although not absolutely so, to *cis*-9-unsaturated acids, especially to oleic acid, independently of their position (Section IV, 8). The enzyme hardly detaches elaidic acid at all, which demonstrates the stereoselectivity of formation of the enzyme–substrate complex[101,112,116]. The non-specific lipases of the castor-oil plant and of Streptococcus aureus are not used in the analysis of glycerides[54,105]. Hypotheses assuming the participation of plant lipases in the synthesis of triglycerides have now been abandoned[41].

5. Structural Analysis of Triglycerides by Mass Spectrometry

Non-enzymic methods for the structural analysis of triglycerides include mass spectrometry (Fig. 5) and also the determination of polymorphism, nuclear magnetic resonance spectroscopy, and infrared spectroscopy (Section V).

The mass spectrum of synthetic 1-myristoyl-3-palmitoyl-2-stearoyl-*sn*-glycerol, obtained on an MS-9 instrument at 170–200°C, exhibited the following peaks: (1) a peak due to the molecular ion M^+ at $m/e = 804$; (2) peaks at 523, 551, and 579 formed by the elimination of RCOO groups from M^+ (where R = St, Pal, or Myr); (3) peaks due to the ions of these acyl groups at 267, 239, and 211; and (4) peaks due to ions formed by elimination of the fragment CH_2OCOR from M^+ (at 509, 537, and 565 respectively). Fig. 5 shows that the intensity due to the ion (peak with $m/e = 509$) resulting from the elimination of $CH_2OCOC_{17}H_{35}$ (the fragment containing the 2-stearate residue from the initial triglyceride) from the M^+ ion was

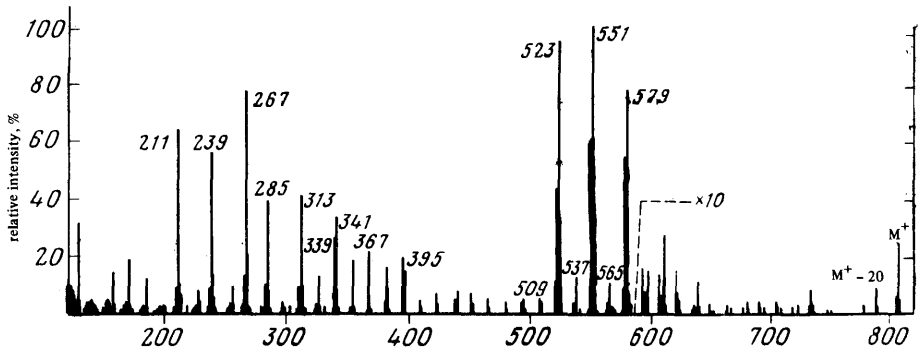


Figure 5. Mass spectrum of 1-myristo-2-stearo-3-palmitin [117].

$CH_2OCO_{13}H_{27}$
|
$CHOCOC_{17}H_{35}$
|
$CH_2OCOC_{15}H_{31}$
$M = 804$

one-third of the intensities of ions with peaks at 537 and 565. Hence the position of an acyl radical in the triglyceride molecule can be established from the relative intensities of the peaks due to $M^+ - CH_2OCOR$. Thus the synthetic triglycerides 2-OlStSt and 1-OlStSt gave different mass spectra. With compounds of molecular weight below 1058 decomposition under the influence of electron impact is not accompanied by thermal decomposition. The mass-spectrometric method is an improvement on lipase hydrolysis with respect to speed and sensitivity of analysis, but as yet it is applicable only to purified individual triglycerides [41,117].

The natural glycerides which have been investigated by mass spectrometry include the optically active triacid triglyceride from the polar fraction of the Chinese oil from Sapium sebiferum, which yields on methanolysis esters of linoleic, linolenic, and deca-2,4-dienoic (10:2) acids. The molecular weight of this glyceride, determined by mass spectrometry, is 920, not the 778 which might have been expected from its fatty-acid composition. The difference of 142 indicates that this compound contains also a residue of a C_8 hydroxy-acid. Since the spectrum did not contain a peak due to $M^+ - CH_2OCOR$ (R = 10:2), it could be assumed that the 10:2 acid was not attached directly to the glycerol. These results helped to establish the structure of the optically active triglyceride, as described in detail below (Section IV, 4).

IV. DETERMINATION OF ABSOLUTE CONFIGURATION OF TRIGLYCERIDES

1. Present-day Position of the Problem of the Absolute Configuration of Fats

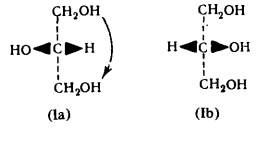
Most of the naturally occurring asymmetric compounds —amino-acids, carbohydrates, terpenes, alkaloids, etc.—are usually enantiomers [35,118]. The structural analysis of triglycerides is often confined to lipase hydrolysis [119], and the stereoisomerism of triglycerides, in contrast to their composition, has been little studied as yet, owing to the difficulty of isolation in a pure form, insufficient development of the preparation of their stereoisomers, and also the fact that modern methods do not usually detect optical activity in the stereoisomers of triglycerides [118].

Optical activity may be expected in asymmetric triglycerides of the type ABC (A = B and A ≠ B) [41], which have now been detected in all natural fats [120]. A racemic mixture of equal quantities of the enantiomers of such glycerides does not possess optical activity. If, however, one enantiomer is completely or partly absent from the mixture, experimental detection of the asymmetric $C_{(2)}$ atom of the glycerol residue is in principle possible [121]. The equivalence or non-equivalence of composition of the acyl groups in positions 1 and 3 in mixtures of optically active glycerides is important for a complete description of the fat and for assessing the reliability of theories of the structure of triglycerides, since many of these theories are based on the hypothesis of a statistical distribution of acyl groups in the 1,3-positions. This problem can also be solved independently of any structural theory [118,121-123].

2. Nomenclature of Stereoisomers of Glycerol Derivatives

The glycerol molecule, which is devoid of optical activity, is usually regarded as symmetrical. The problem arises of how to distinguish between carbon atoms 1 and 3, which are differentiated in the exchange reactions of lipids. The Fischer projection formula of glycerol (Ia) in Scheme 4 (where the solid triangles denote bonds directed towards the reader, and the broken lines those directed away from the reader) shows that the halves formed by the plane through the $C_{(2)}$ atom and the HO–H line are not identical, since they cannot be superimposed.

Scheme 4

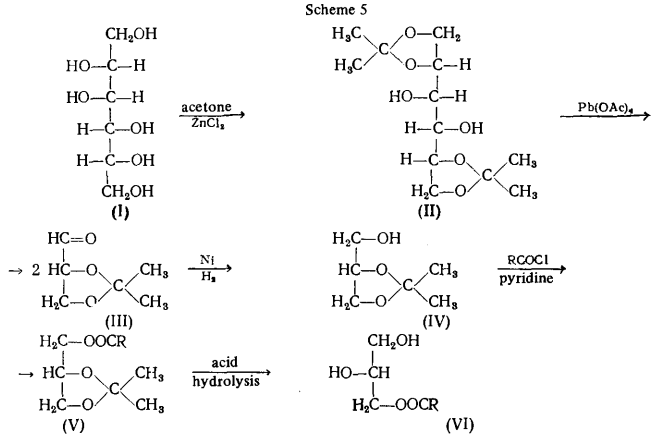


Thus $C_{(2)}$ in glycerol is a *meso*-atom, and glycerol itself has a *meso*-structure, so that it is devoid of rotational symmetry. Indeed, on rotating (Ia) through 180° about an axis perpendicular to the plane of the paper, we obtain (Ib) for glycerol, which cannot be superimposed on (Ia).

The *meso*-structure and the absence of rotational symmetry suggest that the two hydroxymethyl groups will have different fates during exchange reactions with asymmetric reactants (which include all biological reactions), and that they can be distinguished from each other. Thus the biosynthetic replacement of active hydrogen in one of these groups by phosphate, alkyl, acyl, etc. will give a glycerophosphate, batyl alcohol, a 1-monoglyceride, etc. exhibiting optical activity. The steric nomenclature of the carbon atoms of glycerol is therefore important for studying the structure and the biosynthesis of fats [124].

Until recently the Baer–Fischer system was used for denoting the absolute configuration of optically active derivatives of glycerol. In this system a given derivative is assigned to the *D*- or the *L*-series according to which of the two stereoisomers of glyceraldehyde (*D* or *L*) it can be converted into by the least number of reactions. In particular, one stage in such conversion for unsymmetrical mono- and di-glycerides is oxidation of the free primary hydroxymethyl group to an aldehyde group without change in position of the substituents. A non-acylated, phosphate-substituted, radioactively labelled, etc. hydroxymethyl group is always denoted by the Greek letter α and the secondary $CH.OR_{(2)}$ group by the letter β. This system has several drawbacks for structural and biochemical purposes, since it remains obscure whether α denotes the 1- or the 3-position. Baer and Fischer's nomenclature was modified to the so called "conventional" *D*/*L* system.

Scheme 5



This still used the prefixes *D* and *L*, but the positions of substituents were denoted by the numerals 1, 2, and 3, where "1" denotes acylation of a hydroxymethyl group. This system also has defects: for example, according to this nomenclature the phosphorylation product of an *L*-1,2-diacylglycerol (a phosphatidic acid) can be termed either an *L*-1,2-diacylglycero-3-phosphate or a *D*-2,3-diacylglycero-1-phosphate. Therefore this system has now been replaced by others [124-126].

The more complete (*R*)/(*S*) system is based on the sequence in which radicals of different ranks are arranged about the centre of asymmetry [118]. The rank of a given group depends on its position in the arbitrary hierarchy—OH > COOH > ketone > aldehyde > hydroxymethyl > CH_3 > > H, etc. [126] In glycerides longer acyls have priority before shorter acyls, unsaturated before saturated, branched before straight-chain, *cis* before *trans*, etc. A hydroxymethyl group substituted by an acyl of lower rank is numbered "1". In a triglyceride the sequence begins with a group of higher rank—OR at $C_{(2)}$—containing oxygen, and it terminates with the radical of lowest rank—the hydrogen atom at $C_{(2)}$. If the radicals in order of diminishing rank are arranged clockwise in a plane above the $C_{(2)}$ atom viewed from the side opposite to the substituent of lowest rank (the hydrogen atom), the triglyceride belongs to the right-hand or (*R*) configuration; if the opposite is true, it belongs to the left-hand or (*S*) configuration. Thus the optical enantiomers of α-laurodipalmitin (Section IV, 3) are denoted in the (*R*)/(*S*) nomenclature as (*S*)-1-laurodipalmitin (I) and (*R*)-1-laurodipalmitin (II) [118]. The advantages of this system are universality and the absence of any ambiguity in the notation. However, the reactions of glycerol derivatives mostly involve only the 1- and 3-ester bonds. As a consequence, the configurational prefixes (*R*) and (*S*) are often interchanged: thus the product of the phosphorylation of an (*S*)-1,2-diacylglycerol is termed an (*R*)-phosphatidic acid. Little use of the (*R*)/(*S*) system is now made in the nomenclature of lipids [124].

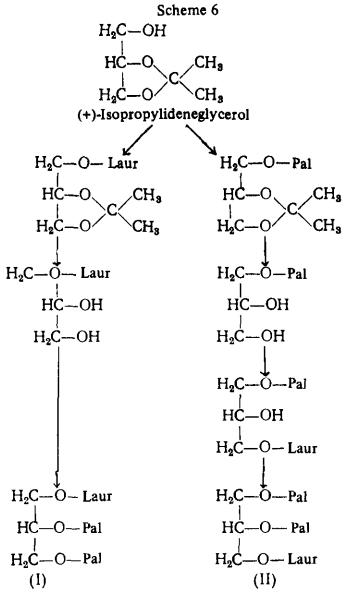
Hirschmann proposed for glycerol derivatives a system of stereospecific numbering with a fixed position of substituents (the *sn*-system), which is now the most widely used for denoting the stereospecificity of triglycerides [124, 126]. If was stipulated that the carbon atoms in the projection formula of glycerol (Ia), in which the substituent of higher rank (the hydroxyl on the *meso*-carbon atom) is always turned to the left, and the hydrogen to the right, should be numbered in the same way as the carbon atoms in *L*-glyceraldehyde, i.e. downwards (I). Thus each primary hydroxymethyl group of glycerol has a definite number in the *sn*-system, and can sometimes be numbered "1" and sometimes "3". Here a triglyceride is termed a 1,2,3-triacyl-*sn*-glycerol, and Baer and Fischer's *D*- and *L*-$\alpha\beta$-diglycerides become 1,2- and 2,3-diacyl-*L*-glycerols respectively. An equilibrium mixture of two enantiomers is denoted in the *sn*-system by the prefix *rac*, e.g. *rac*-1-oleodipalmitoglycerol; if the configuration is unknown the prefix X is used, e.g. X-1-palmitodioleoglycerol. The Commission on Biochemical Nomenclature of the International Union of Pure and Applied Chemistry has now recommended the *sn*-system for general application in denoting the absolute configuration of lipids [124,126].

3. Stereospecific Chemical Synthesis of Triglycerides

Owing to the difficulty of isolating stereoisomers from natural fats for the comparison of synthetic with natural enantiomers, methods have been worked out for the stereospecific chemical synthesis of triglycerides [4,120]. Early syntheses were based on the resolution of racemates of intermediate products by means of *D*-tartaric acid, saccharic acid, or strychnine into enantiomers, which were converted into glycerides without racemisation [4]. Nowadays the preparation starts from the optically active natural compound *D*- or *L*-mannitol. In Fischer and Baer's method for the preparation of an *L*-monoglyceride (Scheme 5) 1,2:5,6-di-isopropylidene-*D*-mannitol (II), obtained by treating *D*-mannitol (I) with acetone in the presence of zinc chloride, is converted by oxidative cleavage at the 3,4-hydroxyls with lead tetra-acetate into two molecules of isopropylidene-*D*-glyceraldehyde (III), which is reduced to *D*(+)-isopropylideneglycerol (IV), and this is esterified in the 1-position with an acid chloride to yield the 3-acyl-*L*-glycerol (VI) after the acetone residue

in (V) has been removed by hydrolysis. The 1-acyl-*L*-glycerol is prepared similarly from *L*-mannitol[4]. The stereoisomeric monoglycerides are converted into triglycerides (Section II, 3).

Scheme 6



Scheme 6 shows the synthesis of 1-lauroyl-2,3-dipalmitoyl-*L*-glycerol ((−)(*S*)-1-laurodipalmitin) (I) and 1,2-dipalmitoyl-3-lauroyl-*L*-glycerol ((+)(*R*)-1-laurodipalmitin) (II). Physical methods proved that the products were indeed optical enantiomers[118]. In the stereospecific synthesis of 1,2-dipalmitoyl-3-sorbin the free hydroxyl in (IV) was protected with benzyl, which was removed by hydrogenolysis; the triglyceride obtained was compared with the naturally occurring compound from the oil of S. sebiferum. For the measurement of optical rotation under conditions excluding acyl migration, the 1,2- and 2,3-diglycerides obtained by lipase hydrolysis of the asymmetric triglycerides were acylated with sorboyl chloride or converted into the trimethylsilyl derivatives[120,123]. Triglycerides are synthesised not only from synthetic monoglyceride enantiomers but also from 1,2-diacyl-*L*-glycerols obtained by the action of phospholipase C on egg lecithin[125,127].

4. Physical Methods for Determination of Absolute Configuration of Triglycerides

The primary physical method is polarimetry, since many glycerol derivatives—glycerophosphates, batyl alcohol, monoglycerides, diglycerides, trityldiglycerides—exhibit appreciable optical rotation[4,35,118,123]. Among triglycerides only those containing one or two residues of aromatic acids or volatile aliphatic acids have shown rotation: the *L*-forms of these glycerides are laevorotatory, and the *D*-forms dextrorotatory. This coincidence of the configuration and the sign of the rotation is probably fortuitous: the corresponding 1,3-diglycerides do not exhibit such coincidence[118]. The higher fatty acyls, which differ little in chain length and structure, give rise to such weak optical activity in the enantiomeric triglycerides that it cannot be detected by polarimetry even in the ultraviolet. Acylation of optically active *D*(+)-1,2-diolein ($[\alpha]_D^{20} = +1.73°$) in the 3-position at once removes the optical activity[4,34,35,118,120,121,123]. The dispersion of optical rotation at 300–600 nm in synthetic 1,2-dipalmito-3-laurin is 4% of the value in 1-monopalmitin and is opposite in sign of rotation[118]. Thus the absence of rotation in an unsymmetrical triglyceride still does not suggest that it is racemic in composition. Enantiomeric triglycerides, which do not directly exhibit optical rotation even in ultraviolet radiation, are said to be "cryptoactive"[4,34,35,118].

The strong rotation of dolphin fat and of the oils of the plants S. sebiferum and Sebastiana lingustrina (Euphorbiaceae family) is due to the presence of a centre of asymmetry not in the glycerol residue but in the acyl groups[118,120,128]. The polar fraction of the oil from S. sebiferum is an optically active triglyceride ($[\alpha]_D^{20} = -21.9°$). Treatment with lithium tetrahydroaluminate followed by acetic anhydride with the formation of triacetin and the acetates of the aliphatic alcohols shows that this glyceride contains equal quantities of linoleate and linolenate together with 31.5% of deca-2,4-dienoic acid. The optical activity of the glyceride disappeared after hydrogenation, and ethyl decadienoate was inactive. The first paper on this topic attributed the optical activity to the presence of decadienoic acid in the 1- or 3-position of the glyceride, near the potential centre of asymmetry, the $C_{(2)}$ atom of glycerol[128]. However, the value of $[\alpha]_{546}^{20}$ for the synthetic analogue—the 1,2-dipalmitate 3-hexa-2′,4′-dienoate of *sn*-glycerol—was only −3.60°. A later investigation of the glyceride of S. sebiferum by infrared and nuclear magnetic resonance spectroscopy together with mass spectrometry established[129] its true structure as

Linolenoyl.O.CH_2.CH(O.Linoleoyl).CH_2.O.CO.$[CH_2]_3$.CH:CH*:CH.CH_2.O.CO.CH:CH.CH:CH.$[CH_2]_4$.CH_3.

The decadienoic acid residue was proved to be attached not to the glycerol residue but to the acyl of an optically active C_8 hydroxy-allenic acid. Thus the centre of asymmetry C* of the triglyceride occurs not in the glycerol residue but in the aliphatic chain of a C_8 acid[128,129].

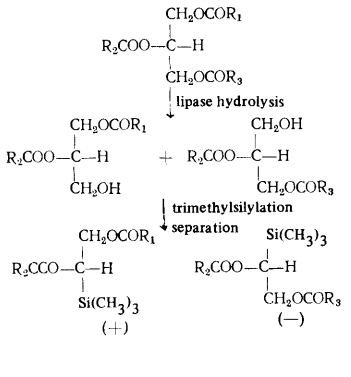
Among natural triglycerides only the *L*-1,2-diacyl-3-acetins—the main components of the seed oils of Euonymus verrucosus, Impatiens edgeworthii, and other plants of the families Celastraceae, Rosaceae, Balsaminaceae, Lardizabalaceae, and Ranunculaceae—have shown measureable optical activity due to asymmetry of the glycerol residue. After hydrogenation the oil contained *L*-1,2-palmitostearo-3-acetin and *L*-1,2-distearo-3-acetin; their mixture had $[\alpha]_{350}^{25°} = 1.9°$, and the main infrared band was located at 8.1 μm, indicating the presence of an acetate group. The optical activity of the stereoisomeric glycerides does not vanish on hydrogenation, storage under ordinary conditions for 6–7 years, or heating to 170°C with the exclusion of acyl migration and oxidation. However, the optical activity was lost after randomisation, which proves that the centre of asymmetry is situated in the glycerol residue of these triglycerides[130–132].

The identification of enantiomers and racemates and establishment of the configuration of cryptoactive triglycerides by physical methods requires the isolation and careful purification of individual glycerides, and these should be examined in the form of crystals. Study of the

piezoelectric excitability of three synthetic triglycerides between electrodes at the a.c. frequency showed that a piezoelectric effect occurred only with enantiomers, but was absent in a racemate. Differences in melting point between the racemate and enantiomers are too small for identification of the latter, and it is therefore necessary to obtain phase diagrams of mixtures of a triglyceride of unknown configuration with each of the corresponding enantiomers [34,118].

It is more convenient to determine the stereoisomerism of triglycerides by X-ray examination. Stereoisomers give the same diffraction pattern, which differs from that due to the racemate. To determine the configuration of 2-OlPalSt of cocoa butter, therefore, the X-ray photographs of a synthetic racemate and of the natural glyceride were compared: the identity of the patterns showed that the natural product was a racemate. If such coincidence had not occurred, it would have been necessary to obtain the X-ray diagram of a mixture of the natural glyceride with one of the synthetic stereoisomers: if the pattern remained unchanged, the cocoa glyceride was idential with this stereoisomer; if not, it was identical with the other stereoisomer [118].

Scheme 7



5. Qualitative Detection of Optical Activity of Triglycerides by Chemical Methods

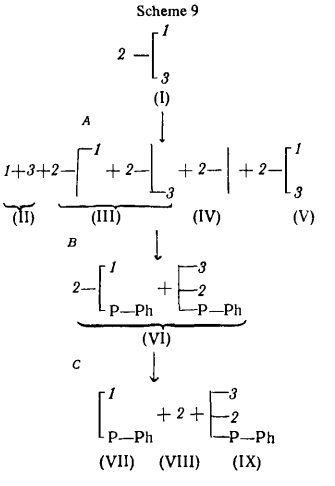
The detection of optical activity e.g. in vegetable SatUnsatUnsat triglycerides, requires their conversion by lipase hydrolysis into a mixture of the 1,2- and 2,3-diglycerides; the diglyceride acetates obtained by acetylation can be oxidised at the double bonds with a solution of potassium permanganate and periodate to give a mixture of AcAzSat and $AcAz_2$ triglycerides. The presence of rotation in this mixture will suggest non-equivalence in the composition of the acids at positions 1 and 3 in the original SatUnsatUnsat glycerides [41].

Appreciable rotation ($[\alpha]_{546}^{20°} = +3.7°$) was observed in synthetic 1,2-dipalmitoyl-3-sorboyl-*L*-glycerol. It was therefore suggested that polarimetry of appropriate derivatives of 1,2- and 2,3-diglycerides—products of the lipase hydrolysis of the fat—could be used to establish the presence of stereoisomers in a fat [41,120]. Polarimetry was applied to the trimethylsilyl ethers of the diglycerides, since they surpassed both sorbic esters and the diglycerides themselves in angle of rotation $[\alpha]$; furthermore, migration of acyl groups was excluded by their use. The standard was the trimethylsilyl ether of *L*-1,2-dipalmitoylglycerol, with $[\alpha] = +4.7°$. The SatSatUnsat and UnsatUnsatSat glycerides of several natural fats were split with lipase, and measurements of the angle of rotation $[\alpha]$ were made on the stereoisomers of trimethylsilyl-sn-1,2- and -2,3-diglycerides of different acid composition obtained by thin-layer chromatography of the silver complexes (Scheme 7). All the triglycerides studied were active, the angles of rotation of enantiomers being opposite in sign; however, all fractions had lower values than the synthetic standard (Scheme 8). In this way we can first establish the absolute configuration of a glyceride or its predominant stereoisomer [123].

Scheme 8

Fat	Triglycerides	[α] of trimethylsilyl derivative of 1,2-diglycerides		[α] of trimethylsilyl derivative of 2,3-diglycerides		Absolute configuration *sn*-system	Absolute configuration Ingold
Pork fat	SatSat Unsat	SatSat	+1.6°	UnsatSat	-1.3°	Sat—{Sat, Unsat}	(*R*)
Palm oil	Unsat Unsat Sat	UnsatUnsat	+2.5°	SatUnsat	-2.3°	Unsat—{Unsat, Sat}	(*S*)
Myristica malabarica fat	Unsat Unsat Sat	UnsatUnsat	+0.5°	SatUnsat	-3.9°	Unsat—{Unsat, Sat}	(*S*)
Cocoa butter	Unsat Unsat Sat	UnsatUnsat	+1.0°	SatUnsat	-3.2°	Unsat—{Unsat, Sat}	(*S*)

Scheme 9



6. Quantitative Determination with Phospholipase A of the Stereoisomerism of a Natural Mixture of Triglycerides

Brockerhoff's method [125] is based on the steric and positional specificity of lipolytic enzymes (Scheme 9, where *1–3* are acyl groups of fatty acids). Lipase hydrolysis (*A*) of the triglyceride (I) gives the free fatty acids (II), a racemic mixture of *sn*-1,2- and *sn*-2,3-diglycerides (III), a monoglyceride (IV), and unchanged triglyceride (V). The mixture (III) is phosphorylated (*B*) with phenyl phosphorodichloridate to give a mixture of *L*- and *D*-phosphatidylphenols (VI), which is hydrolysed at the 2-position (*C*) by means of stereospecific phospholipase A

(EC 3.1.1.4), to yield *L*-lysophosphatidylphenol (VII), a free fatty acid (VIII), and an unhydrolysed 2,3-diacyl-*L*-glycerol 1-phosphate (IX) (*D*-phosphatidylphenol in Fischer's nomenclature). The composition of the acyls in the 1,2- and 3-positions of the triglycerides can be calculated independently from the acid composition of the initial, intermediate, and final products.

If acyl migration occurs and hydrolysis is specific with respect to fatty acids, the acid composition of the 1,3-positions in the diglycerides will not be identical with that of the original fat [41]. Hydrolysis of *D*-, *L*-, and *DL*-dipalmito-olein by lipase showed that acyl groups *1* and *3* were detached simultaneously and at the same rate, and the diglycerides obtained were optically inactive. The [Pal]/[Ol] ratio in the free fatty acids and in the diglycerides in the reaction mixture (1 : 1 and 3 : 1 respectively) corresponded to the theoretical value [133]. During hydrolysis on a macro-scale stearate was split off more slowly than other acyl groups [68]. To ensure statistical hydrolysis hexane was added to the medium (Section III, 2); this weakened the van der Waals forces that retained selectively the longer and less curved acyl groups on the surface of the fat micelle [9,125]. The detachment of polyunsaturated acids having $m = 20–22$ lagged behind even with hexane, so that they accumulated in the diglycerides. Therefore "marine" fats and also pork fat and maize oil were deactivated with a Grignard reagent (0.06–0.12 M CH_3MgBr in ether): symmetrical monoglycerides and diglycerides showed considerable changes in composition owing to migration of the acyl groups, but 1,2(2,3)-diglycerides corresponded in composition to the original fat, and could be used for stereospecific analysis [9,41,107,134–136]. The composition of the acids of 1,2(2,3)-diglycerides, obtained by hydrolysis on a macro-scale [125,137], differed markedly, by an increased content of saturated acyl groups, from that calculated theoretically. A micro-method of hydrolysis gave better agreement [47,134]. It is possible that statistical hydrolysis is ensured by a diminished calcium-ion level and an increased enzyme content in the reaction mixture [41].

In Brockerhoff's method the diglycerides obtained by hydrolysis (yield 20–30%) were separated into 1,2(2,3)- and 1,3-diglycerides by chromatography on silica gel impregnated with boric acid; in the presence of phenyl phosphorodichloridate, ether, and pyridine at 0°C the 1,2(2,3)-diglycerides were converted into phosphatidylphenols, whose triethylammonium salts were hydrolysed with phospholipase A in ether at pH 7.5 in the presence of calcium chloride. The reaction products were separated by chromatography on an adsorbent impregnated with boric acid, and the acid composition of each fraction was determined by gas chromatography [9,125,135,136]. The compositions of positions 1, 2, and 3 are reliable only if the analytical results show the following equalities: (I) = (V), (III) = (VI), and (IV) = (VIII) (Scheme 9); these indicate that hydrolysis by lipase and by phospholipase has occurred statistically and without isomerisation. The compositions of positions 1 (VII) and 2 (IV) and (VIII) are determined directly; the acid content in the 3-position is calculated in two ways, as either 3[(I) – (IV) – (VII)] or 2[(IX) – (IV)]. An absolute divergence of 4% is acceptable when [A] ≥ 40%, not more than 3% with 10–35%, and at most 2% when [A] < 10%; the error in the calculation does not usually exceed ±2%, and only with difficultly hydrolysable saturated fats does it increase to 8%. [9,10,119,125,136] However, if the results show good reproducibility, only fractions (I), (IV), (VII), and (IX) are analysed [9]. Brockerhoff's method has been tested on synthetic and semi-synthetic triglycerides [125].

Direct analysis of the composition at the 3-position was accomplished by converting the 1,3-diglycerides, obtained by deacylating the fat by means of a Grignard reagent, into *L*-2-phosphatidylphenols and splitting the latter at position 1 with phospholipase A. The resulting lysophosphatides corresponded in acid composition to the 3-position of the initial fat [135].

7. Determination of Absolute Configuration of Individual Triglycerides

In all the fats studied, positions 1 and 3 differ in composition. This proves indirectly the presence of stereoisomeric triglycerides, but does not indicate their nature [123]. However, even identity of composition at positions 1 and 3 in a mixture of triglycerides would not necessarily prove that all the glycerides in the fat were racemates. Thus the ratio of palmitoyl to stearoyl at positions 1 and 3 is unity for the equimolecular mixture—(*R*)-PalOlSt + (*S*)-PalPalSt + (*R*)-PalOlSt + (*S*)-PalPalSt + (*S*)-PalOlSt + (*R*)-PalPalSt—although this mixture contains one-third of the racemate 2-OlPalSt plus one-third of the racemate 2-PalPalSt plus one-sixth of the enantiomer (*R*)-PalOlSt plus one-sixth of the enantiomer (*S*)-PalPalSt. Therefore the absolute configuration can be assessed only by analysing individual glycerides or simple mixtures in which a certain acyl group (e.g. palmitoyl in (*S*)-PalOlSt + StOlSt) is present only in one of the outer positions in one of the glycerides [118].

The problem of analysing the configuration of mixtures and individual types of diacid (A_2B) triglycerides has now been solved, at least in principle: metamers having the same m and e but different numbers of saturated acyls (e.g. StStLinoleoyl and StOlOl) can be separated; the proportions of stereoisomers in A_2B are easily found from the content of the acid B at positions 1, 2, and 3 in the mixture AAB + ABA + BAA. Establishment of the configuration of triacid glycerides—i.e. the proportions of the six possible stereoisomers ABC, ACB, BAC, BCA, CAB, and CBA—is a more complicated matter. From the composition of the acids at positions 1, 2, and 3 it is possible to find the proportions of any pairs of isomers, e.g. pairs with respect to the content of acid A:[122]

(I)				(II)		
AA	BC	BC		AB	AC	BC
BC	AA	CB		BA	CA	CB
CB	CB	AA		PP	PP	PP
				x	y	z

An additional parameter is necessary for calculation of the quantity of each stereoisomer in the mixture (I), and can be obtained by separating the intermediate products in the analysis according to the acid composition: the glyceride ABC is hydrolysed with lipase, and 1,2(2,3)-diglycerides are isolated; the 1,2-diglycerides are converted into phosphatidic acids by means of stereospecific diglyceride kinase, and the acid composition of each position is found by Brockerhoff's method modified by first separating the phosphatidic acids into pairs of stereoisomers according to acid composition (II). The proportions of the pairs x, y, and z are equal to the proportions of the acids C, B, and A respectively in the 3-position. The proportions of isomers within a pair are determined by hydrolysis with phospholipase A [138].

8. Use of Other Enzymes than Phospholipase A for Analysis of Stereoisomerism of Triglycerides

If the glyceride ABC contains oleate, the additional parameter for estimating the stereoisomers can be obtained by means of the lipase of G. candidum (Section III, 4) together with Brockerhoff analysis; the 1,2(2,3)-diglycerides obtained by the elimination of oleate from the 1(3)-positions are converted into phosphatidylphenols, and the ratio of stereoisomers in a pair is determined by hydrolysis with phospholipase A[139].

Other stereospecific enzymes of lipid metabolism are suitable for the analysis of stereoisomerism. A racemic mixture of phosphatidylphenols can be resolved by hydrolysis with phospholipase C, which is specific to the L-isomer[9]. The triglycerides of rat liver have been analysed by means of the diglyceride kinase of Escherichia coli, which converts 1,2-diglycerides, obtained by lipase hydrolysis, 25 times as rapidly as 2,3-diglycerides into phosphatidic acids[137,140,141]. The contents of each acid at positions 1, 2, and 3 were calculated by means of the formulae

$$[A]_1 = (2[A]_{Phtd} - [A]_{MGl}) : 3;$$
$$[A]_2 = ([A]_{MGl}) : 3;$$
$$[A]_3 = [A]_{TGl} - (2[A]_{Phtd}) : 3,$$

where $[A]_{TGL}$, $[A]_{MGl}$, and $[A]_{Phtd}$ are the contents of acid A in the initial triglycerides and in the 2-monoglycerides and phosphatidic acids obtained from them. These equations hold only if the fatty-acid composition of the 1,2(2,3)-diglycerides obtained by lipase hydrolysis corresponds to the calculated composition (Section IV, 6) and substitution of $[A]_{1,2(2,3)}$ for $[A]_{1,2}$ in the equation gives the same acid composition in 1- and 3-positions. The differences observed indicate the minimum error of the method. These differences are often considerable, which is evidence of the fatty-acid selectivity of lipase hydrolysis. It is therefore necessary in each experiment to ensure agreement between experimental and theoretical acid compositions[134].

V. POLYMORPHISM OF TRIGLYCERIDES

1. Lattice Structure and Phase Transitions of Triglycerides

The phenomenon of polymorphism was discovered as early as 1821 by Mitscherlich. The various forms of a given compound differ appreciably in crystal structure, lattice parameters, melting point, density, and other properties, but have the same composition and chemical structure and, unlike position isomers, give an identical liquid or gaseous phase. The crystalline modifications of carbon—graphite and diamond—provide an inorganic example of polymorphic forms. Organic compounds also exhibit polymorphism, especially long-chain aliphatic compounds, including natural glycerides. Before the 1930s the triple melting points of a triglyceride, discovered more than a century earlier, were attributed to the presence of a series of position isomers; only Malkin proved that the melting anomalies were due to differences in the crystal lattice. When a solidified melt (the polymorphic α-form) of a simple Sat_3 glyceride is heated slowly, it melts, and then solidifies again with the evolution of heat, to form the stable β-form or an intermediate β'-form; the latter appears when the melt is maintained at 1–2 deg above the melting point of the α-form. The direction of these transitions, which may not be accompanied by fusion, is from less stable modifications, whose formation requires a minimum change in free energy of the lattice, to thermodynamically more stable polymorphic forms having little free energy. The principal α-, β-, and β'-forms of triglycerides differing in composition and structure have similar properties, since the acyl chains play the decisive part in the polymorphism. However, new, additional polymorphic forms are continually being found in the huge variety of natural fats, and therefore a classification and a nomenclature have not yet been established for the latter. The direction and the products of polymorphic transitions depend on the purity of the material, the presence and nature of a crystal seed, the solvent, the pressure, the temperature, its rate of change, etc. Thus the crystalline, thermal, X-ray diffraction, and other properties of a triglyceride under given environmental conditions can be assessed only after establishment of the polymorphic form in which the compound is then present. Several reviews have appeared on the polymorphism of triglycerides[4,142-154].

X-Ray diffraction indicates that aliphatic chains are zigzag structures with rectilinear axes, in which the angle between the carbon–carbon bonds is 109°28', and the increase in the length of an acyl residue accompanying expansion of the latter by a methylene group is $a = 1.28$ Å.[4] If the temperature is not sufficiently low, close approach of chains to one another is difficult, and the triglycerides remain liquid, without an ordered structure. As the acyls come closer together on cooling, van der Waals forces of attraction become effective between carbon atoms of adjacent chains: i.e. the triglycerides crystallise[146,147].

Crystals formed by identical aliphatic molecules, whose ends differ in polarity, contain a mainly parallel arrangement of chains forming a kind of "palisade" and usually a crystalline double layer by means of the hydrogen bonds of the polar groups. A vivid model of this arrangement would be two bundles of very large numbers of matches, where the heads represent methyl groups and the free ends the polar groups: one bundle is placed with the heads in a plane, and the other with the free ends on the first bundle. Thus the double layers of molecules are bounded by non-polar "methyl" planes, the distance between which is termed the long spacing L (in Å). The value of L found from X-ray examination enables us to determine the number of chains constituting the long spacing[4].

If the double layers $2m$ long are perpendicular to the methyl planes, $L = 2m$. Layers having L which are multiples of $3m$ or $4m$ occur in crystals of mixed glycerides. Mostly, however, $m < L < 2m$, and the angle of tilt between the axes of the chains and the planes $\beta_X < 90°$. The variation in β_X between different crystalline forms is a principal cause of the polymorphism of triglycerides: decrease in β_X strengthens contact between their more polar ester groups, and hence improves the stability of the polymorphic forms[143,146,149]. The value of L for a given form varies with the acid composition of the triglycerides. The hypothesis that decrease in L is due, not to tilting of the chains, but to erratic secondary bends[149], has not yet been proved experimentally.

The parallel chains in triglycerides form a unit cell—a right prism or an oblique prism—whose width, termed the short spacing S, is determined by the mode of packing of chains in the crystal lattice. This is the other main reason for the polymorphism of glycerides. In contrast

to L, values of S for a given form are almost constant and independent of m.[143,147,154]

Fig. 6 shows a model consisting of two pairs of chains in the unit cell of stearic acid[4]. A triglyceride unit cell containing two molecules is more complicated: since the axis of one acyl forms an angle of 180° with those of the other two acyl groups (Fig. 6), each chain in the lattice coincides with the long axis of the four-sided prism formed by the other four chains (Fig. 7)[149].

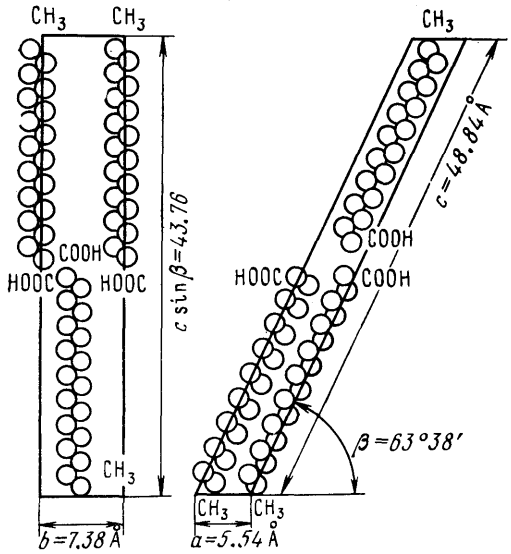


Figure 6. Unit cell of crystal of polymorphic β-form of stearic acid[4]: a and b are short interplanar spacings; $c \sin \beta_X$ is the long interplanar spacing.

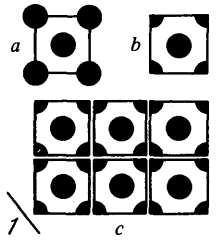


Figure 7. Unit cell of triglycerides[149]: *a*) cross-section; *b*) cross-section with two molecules (or double molecules) belonging to the cell; *c*) cross-section through crystal.

Fig. 8 illustrates possible configurations of the molecules in triglyceride crystals. It was assumed initially that the fork configuration predominates, and later that a chair configuration will give denser packing. X-Ray examination of a single crystal of the β-form of trilaurin has now shown (Fig. 9) that a rod configuration gives the most economical packing with the smallest free energy, without contradicting the principles of symmetry[143,144].

The crystal is seen to consist of $2m$ layers of rodlike molecules in triclinic packing: two acyl groups are located in a straight line, while the third (it is not yet known which—whether the middle or one of the outer acyl groups) is located at their side and parallel to them. Good agreement is evident between values of the angle β_X found from the X-ray photograph and calculated from L (62°7′ and 61°35′ respectively). The rod form ensures also the formation of $3m$ and $4m$ layers in the crystal (Fig. 8)[143,149]. The shape of the molecules in the other main modifications (α and β') has not yet been ascertained[151].

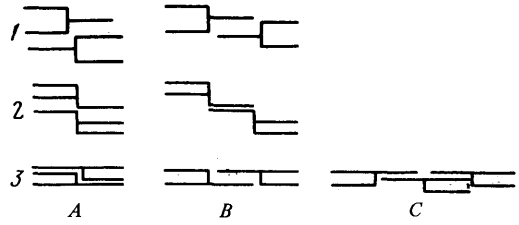


Figure 8. Possible configurations of triglycerides in crystals: 1) fork; 2) chair; 3) rod. Long spacing multiple of: *A*) $2m$; *B*) $3m$; *C*) $4m$.

Phase transitions in heterogeneous systems may be either enantiotropic, i.e. occur reversibly in both directions without melting as the temperature is varied, or monotropic, these being irreversible processes accompanied by loss of free energy in the direction of greater stability, and regeneration of the unstable from the stable form requires intermediate fusion. The phase transitions of triglycerides are mainly monotropic[143].

Pure triglyceride preparations, uncontaminated by homologues of closely similar composition or structure, are necessary in order to obtain sharp polymorphic transitions and forms having definite properties. Thus low-resolution nuclear magnetic resonance spectra indicate the absence of a liquid phase below the melting point in pure specimens of trilaurin and tristearin, but this phase appeared long before melting in contaminated crystals of the β-forms of OlPalPal, PalOlPal, PalOlOl, and StOlSt.[152,161]

In supercooled melts the dependence of the logarithm of the viscosity on the reciprocal of the absolute temperature usually shows a break in the curves immediately below the melting point of the β-form, indicating intensification of aggregation of the glycerides by parallel packing. On the other hand, the crystalline structure of a triglyceride is partly preserved immediately after melting: on rapid cooling, this melt immediately crystallises. After the partly ordered structure of the liquid phase has been destroyed by being kept at a temperature 20 deg above the melting point for 30 min, crystals form slowly[153,160,164]. When tripalmitin is crystallised from a solvent, the properties of the resulting crystals of the β-form depend on the nature of the latter[157].

Table 4 indicates the conditions under which the main polymorphic forms of simple Sat_3 triglycerides are obtained[143,146], together with several methods for investigating the polymorphism. The early methods involved determining melting points in capillary and differential

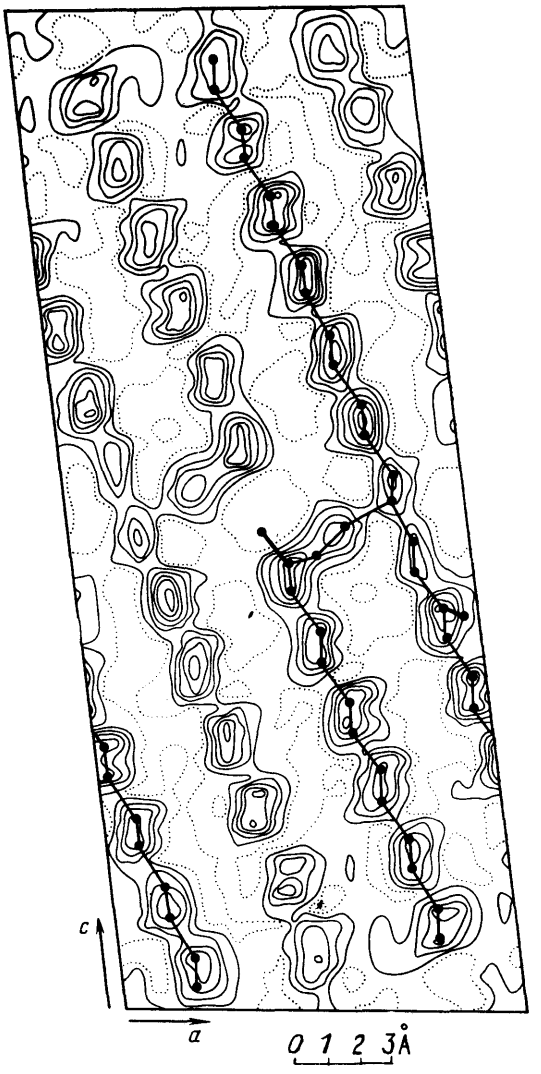


Figure 9. X-ray electron density diagram of polymorphic β_L form of trilaurin[143].

thermal analysis, consisting in recording continuously the evolution of heat during solidification, or its absorption during fusion, from the curves for the difference in temperature between the surrounding medium and a sample of the triglyceride during cooling or heating respectively[4,5,33,155-163]. Dilatometry records the increase in specific volume V_S (in ml g^{-1}) of the triglyceride at a phase transition point—the melting point—and also the equal but opposite change (contraction) at the freezing point. Both processes are recorded as functions of temperature[148,156,158]. Heating the α- and β-forms of tripalmitin in a microdilatometer at a rate of 6.4 deg min^{-1} (Fig. 10) led to the discovery that the differences between initial and final specific volumes when the β-form melts are due to the formation of an intermediate β'-form when the melt sets. The setting of trilaurin and tristearin melts led directly to the metastable α-form, whose stability increased with increase in m; heating the latter resulted in appearance of the β-form[157].

Polymorphic transitions governed by temperature can be detected by periodic determination of the number and magnitude of L and S characteristic of particular forms of a given glyceride, and also from the X-ray diffraction diagrams of the powdered crystals or a large single crystal (Fig. 9)[154,159,164,165]. Changes in the packing of chains on passing from an unstable to a stable polymorphic form can be detected by infrared spectroscopy (Fig. 11) from the characteristic skeletal vibrations at 2–15 μm (5000–600 cm^{-1}).[147,149,155,159,162] Finally, low-resolution nuclear magnetic resonance spectroscopy evaluates the rotational mobility of the acyls in a triglyceride lattice, detects the thermal $\alpha \rightarrow \beta$ transition in tristearin, and enables small quantities of liquid phase in triglyceride crystals to be determined to ±2%. This method is more effective than dilatometry, which gives only the relative content of the solid phase[161,164].

Table 4. Properties of main polymorphic forms of simple saturated triglycerides*.

Notation of form in nomenclature of:			
Malkin	Vitreous	α_M	β_M
Lutton	$a_L^{\bullet\bullet}$	$\beta'^{\bullet\bullet}_L$	$\beta_L^{\bullet\bullet}$
Gunstone	V	U	T
Angle β_X, degrees	90	68	64
Alternation of m.p. of "even" and "odd" homologues (°C)	absent(54.5)	absent(65.0)	absent (71.5)
Short spacing, Å	4.15	3.8 4.2	4.6
Value of c (Å) for calculating long spacing from Gunstone's eqn. with even m and			
L multiple of $2m$***	4.9	4.3	3.7
L multiple of $3m$	—	—	8.4
Packing of chains	hexagonal	orthorhombic	triclinic
Main absorption bands of group V (Table 5), cm^{-1}	720	727, 719 (doublet)	717

*Corresponding data for tristearin given in parentheses.
**Main methods of preparation: α_L by freezing a melt below 0°C; β'_L by freezing a melt at 1–2 deg above the melting point of the α_L form; and β_L by crystallisation from polar solvents or by slowly heating crystals of the α_L form above its melting point.
***In Gunstone's equation $m_A = 0$.

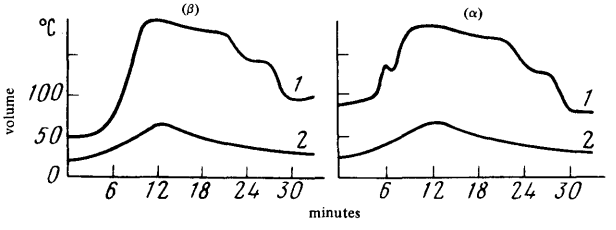


Figure 10. Curves for polymorphic forms (stable β and metastable α) of tripalmitin[156]: 1) dilatometric; 2) temperature.

2. Polymorphic Forms of Trisaturated Triglycerides

The polymorphic forms and several of their properties are given in Table 4;[143,146] fuller information will be found in Markley's monograph[4]. There is as yet no generally

accepted nomenclature for the forms (Table 4). Malkin's early nomenclature, which distinguishes four forms of a given glyceride—vitreous, α, β', and β—in order of rising melting point, is defective, since different forms differing in crystalline structure may have closely similar or even identical melting points [4,145,149]. According to Lutton no vitreous form devoid of crystalline structure actually exists, and there are only three main forms—α, β', and β-characterised by the spacing S (Table 4). [147,154,165,166] To avoid confusion the nomenclature used for a given form is denoted by a subscript indicating the author (α_M, α_L, β'_L, etc.), and the number of chains in L is denoted by a numeral following the subscript (β'_L-2, β'_L-3, etc.). [144,146,151,159]

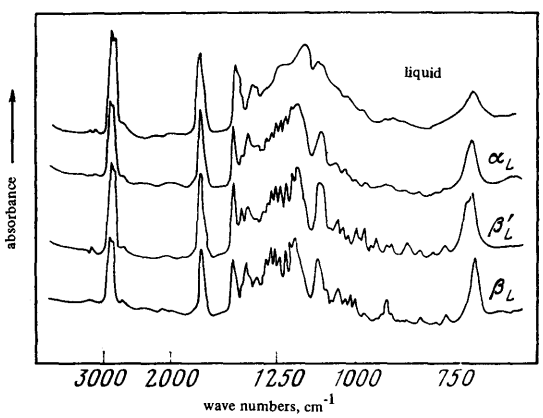


Figure 11. Infrared spectra of polymorphic forms of tristearin [143].

The number and the properties of individual polymorphic forms of triglycerides have been determined also by infrared spectroscopy. The characteristics of the infrared spectra of melts or solutions of simple Sat_3 glycerides are given in Table 5. [33,142,155,159] Solid glycerides are characterised by the intensity and the number of vibrational bands in group V; three types of infrared spectra, corresponding to Lutton's principal modifications, have been found from these sets of bands (Table 4).

In the α_L modification (Table 4), which is formed from the melt, the chains are 5 Å apart, and rotate freely about their vertical axis. The numerous bands due to the α_L form at 1250 cm^{-1} prove that it is crystalline, not vitreous as assumed by Malkin. In the glycerides trilaurin and above, which have a stable α_L form, the number of these bands is $\frac{1}{2}m$, which enables the length of the acyls in the glycerides to be determined from the infrared spectrum [143].

The properties of the β'_L form (Table 4) indicate the usual orthorhombic packing of two types of tilted chains, in mutually perpendicular planes. Formation of this modification of tristearin has been observed on crystallisation from paraffin oil [143,152].

Finally, the β_L form (Table 4) corresponds to triclinic packing, in which all planes of the zigzag aliphatic chains are mutually parallel. The chains themselves are more stable and are packed more densely than in the α_L form. In tristearin the amplitude of rotational oscillations of the chains about the vertical axis does not exceed 17°. [143]

The nomenclatures of Malkin and of Lutton do not enable triglycerides to be compared with other aliphatic compounds with respect to the properties of their polymorphic forms. In Gunstone's nomenclature [146] the polymorphic forms of long-chain saturated compounds are divided into five groups according to the angle β_X, triglycerides occurring in the first three groups V, U, and T (Table 4). The value of L in crystals of mono-, di-, and tri-acid Sat_3 triglycerides ABC (the acyl group B always occupies the 2-position), being a linear function of the chain length m, can be calculated by means of the equation $L = 1.28 \sin \beta_X (m_A + mB + mC) + c$, where m_A, mB, and mC are the numbers of carbon atoms in the acyls A, B, and C, while c is the constant increment in L (in Å) representing the length of a glycerol residue and the zone of contact of the ester groups. Table 4 gives values of c for $2m$ and $3m$ layers of simple and mixed triglycerides containing acyl groups A, B, and C of different lengths. For a double ($2m$) layer m_A in Gunstone's equation is regarded as zero. Good agreement was found between calculated values of L and those obtained from X-ray data [146].

Table 5. Main absorption bands in the infrared spectrum of simple trisaturated triglycerides.

Group of vibrations	I	II	III	IV	V
Absorption bands, cm^{-1}	3030—2967	1751—1733	1464—1453, 1383—1361	1179—1166	1261—1250, 730—717
Vibrating group	C—H	C=O in COOR	CH_2	C—O	CH_2
Mode of vibration	stretching	stretching	scissor deformation	stretching	rocking deformation

Gunstone's numenclature showed for the first time that each polymorphic form is characterised by a definite angle of tilt, but it is unsuitable for calculations on unsaturated glycerides and does not allow for additional polymorphic forms of simple Sat_3 glycerides having the same value of β_X as the principal modifications [151]. The sub-α_L form is one such additional modification: it is produced without fusion from the α_L form of tristearin at −50°C, is converted reversibly into the α_L form, and is identical with the β'_L form in all properties other than the angle $\beta_X = 90°$. Crystallisation from a solvent or heating of the α_L form sometimes results in the appearance of a series of stable β_L forms, identical in diffraction pattern but differing in β_X. In contrast to "even" triglycerides, "odd" acids are stable not in the β_L but in the β'_L form [142,143,152,159].

Attempts to allow for the additional forms were made by Hoerr and by Larsson. Hoerr's nomenclature allows for four modifications—α, β', intermediate, and β—in order of rising melting point. The intermediate modification, which appears when the α form is heated, has since proved to be a mixture of equal quantities of orthorhombic and triclinic forms [146,148]. According to Larsson, (1) forms having a single value of $S = 4.15$ Å are denoted α; (2) forms having two values of S (4.2 and 3.8 Å) and a doublet at 720 cm^{-1} are denoted β'; and the symbol β is applied to all forms which do not correspond to criteria (1) and (2), the presence of several such forms of a given glyceride being indicated by β_1, β_2, etc. in order of decreasing melting point. According to Larsson all planes of the zigzag chains are parallel in β forms, mutually perpendicular in β' forms, and show no definite regularity of arrangement in α forms [151].

Lutton's nomenclature, in spite of its defects, has remained the most acceptable up to the present. It comprises three main forms of simple Sat_3 glycerides—unstable α_L, intermediate β'_L, and stable β_L—which must be regarded as sets of crystalline modifications that have closely similar properties but are not identical. Further research is required to achieve a complete classification [143].

Table 6. Polymorphic forms of some di- and tri-acid saturated triglycerides.

TGl	Δm	Principal forms			Additional forms	Infrared spectrum resembles	Remarks
		α_L-2	β'_L-2	β_L-2			
PalStSt	+2	+	+	+	β_L-3	StStSt	(*a*)
StPalPal	+2	+	+	+	ditto	PalPalPal	
StPalSt	−2	+	−	+	»	StStSt	(*b*)
PalMyrPal	−2	+	−	+	»	PalPalPal	(*b*)
PalStPal	+2	+	+	−	»	PalPalPal	(*c*)
MyrPalMyr	+2	+	+	−	»	MyrMyrMyr	(*c*)
StMyrSt	−4	+	+	+	β'_L-4	StStSt	(*d*)
StLaurLaur	−6	+	+	−	β'_L-3, β_L-3		

(*a*) β'_L and β_L forms equally stable.
(*b*) β_L form the most stable.
(*c*) β'_L form the most stable; β_L form difficult to detect.
(*d*) β_L and β'_L forms have similar values of L.

The polymorphism of diacid and triacid Sat_3 glycerides (Table 6) is extremely individual, depending on the difference Δm between the lengths of the acyls in the 1,3- and 2-positions, the symmetry of the structure, and the presence of an acyl of a lower fatty acid in the 2-position. Sets of polymorphic forms are analogous in homologous series of triglycerides having a certain value of $+\Delta m$ or $-\Delta m$, while symmetrical and unsymmetrical triglycerides of the same composition have identical values of L for $2m$ and $3m$ layers, in good agreement with Gunstone's calculated value (Table 4). In different triglycerides the β_L, β'_L, or α_L form is the most stable. Thus in the glycerides of behenic acid the β'_L forms, not the β_L forms, are stable. Those which are difficult to detect are formed only in the presence of crystals of succinic acid. Mixed glycerides containing two acyls of any acid are almost identical with simple glycerides of the same acid in the number of infrared bands of the α_L form in the region of 1250 cm^{-1}. [142,143,159,166,167] The complexity of the polymorphism increases with the absolute magnitude of Δm (Table 6). An important part in the polymorphism of mixed glycerides containing acyls of volatile acids is played by the carbonyl groups of the latter, with the formation of unique polymorphic forms [4,146,154].

3. Polymorphic Forms of Other Types of Triglycerides

The less studied simple $UnSat_3$ triglycerides in general resemble one another and the corresponding Sat_3 glycerides in the set of polymorphic forms and their properties. Sometimes additional forms occur, e.g. β_L-3 in *cis*-unsaturated triglycerides, which are characterised by bands at 690 and 1660 cm^{-1} due to scissor vibrations of the hydrogen atoms in the *cis*-bond. Triolein resembles tristearin in the main infrared absorption bands of the polymorphic forms at 723 (α_L), 729 and 722 (β'_L), and 722 (β_L) cm^{-1}. When the *cis*-bond is replaced by a *trans*-bond, a band appears at 963 cm^{-1} in all the modifications, and the similarity of the polymorphism with that of Sat_3 glycerides of the same length is still more pronounced. The number of $Unsat_3$ bands at 1250 cm^{-1} is $\frac{1}{2}m$, as with Sat_3 (Section V, 2) [142,144]. Thus unsaturation in simple triglycerides has little effect on polymorphism [4].

Table 7. Properties of polymorphic forms of triglycerides of cocoa butter, 2-OlPalSt and 2-OlStSt.

Form	sub-α_L-3	α_L-2	β'_L-2	β_L-3 (V)	β_L-3 (VI)
Melting point, °C	17	23	27	33	36
Short spacing, A	3.8and4.2	4.2	3.8and4.2	4.6	4.6

Triglycerides of the type SatUnsatSat, constituting ~ 80% of the economically important oil of cocoa beans, have a large set of polymorphic forms. The polymorphism of this oil has been well studied, since it was the chief method of determining the structure of glycerides before the appearance of lipase hydrolysis [168-171]. Crystalline fractions of the oil are identical with a mixture of synthetic PalOlSt, StOlSt, and PalOlPal, while the PalOlSt isolated from the oil coincides with the synthetic triglyceride in melting point, heating curves, dilatometry, diffraction patterns, and infrared spectra of their individual polymorphic forms before and after hydrogenation (Table 7) [33,142]. A mixture of PalOlSt and StOlSt gives three polymorphic forms and differs from either component in rate of conversion of unstable forms, whereas a mixture of StOlSt and StStOl (1 : 3) may give a new crystalline form not present in the initial components [150, 162,165]. Comparison of the polymorphism of StOlSt and StStOl showed no parallelism with the corresponding saturated isomers (Table 6). [168] In homologous series PalPalOl is analogous to StStOl in its polymorphism, and PalOlPal is analogous to StOlSt; in the unsymmetrical $SatUnsat_2$ glycerides StOlOl and PalOlOl, as also with StStOl and PalPalOl, the β'_L-3 form is stable [170]. Nuclear magnetic resonance spectroscopy indicates that the oleate chains in StStOl are less densely packed than are the saturated acyls, and rotate more freely about the axis [4,5, 143,144].

Polymorphism has been most thoroughly studied, apart from StStOl, on the SatSatUnsat glycerides of pork fat [89]. The main component is identical in the properties of its polymorphic forms with OlPalSt [33,150]. Coarse-grained crystals of the β'_L-3 form of this triglyceride appear when pork fat is stored at 27°C, and impair the appearance of the product [172], a phenomenon which is eliminated by transesterification (Section II, 1). [163] In contrast to OlPalSt, StStOl, and PalOlOl, the symmetrical glycerides of pork fat OlStOl and OlPalOl give the forms α_L, β'_L-2, and β_L-3, the last of which is stable [170].

The β_L form is stable in native, hydrogenated, and transesterified beef and mutton fats and in their Sat_3 glycerides [5,163], but the β'_L form, obtained by crystallisation from hexane in the presence of succinic acid, in hydrogenated cottonseed oil, where PalStPal predominates

(Table 6).[172] Transition to the stable polymorphic composition is accelerated by mixing fats rich in SatSatUnsat with fats containing much SatUnsatSat[150,168], and also by keeping at a constant temperature[154]. Thus several vegetable oils acquire a grainy texture during winter storage, owing to the direct transition of the α_L form of the Sat_3 glycerides into the β_L form[4,170].

Study of the polymorphism of natural fats has made progress, and has shown in particular that their structure is not statistical. Further investigations should give a more complete picture of the polymorphic forms of triglycerides, especially the unsaturated compounds, which constitute the major part of the world production of fats, although their polymorphism has been little studied as yet[146]. Determination of the totality of properties of all crystalline modifications of corresponding synthetic and natural triglycerides is important for identification of the latter with respect to composition and structure[5]. The polymorphic properties of a fat are important also for its technical appraisal[164] with respect to consistency, plasticity, graininess, and other properties[142,143].

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The Application of Electrophysical Effects to the Study of the Thermal Decomposition of Solids

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A critical review is presented of work on the thermal decomposition of solid inorganic compounds, based on electrophysical phenomena (electrical conductivity, photoconductivity, contact phenomena, thermo-e.m.f., Hall voltage, and dielectric characteristics). It is shown that electrophysical methods offer an effective approach to the study of the thermal decomposition of solids. The need for further developments in the experimental procedures available, and for comprehensive analysis of the results, is stressed. 156 references.

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1. INTRODUCTION

Studies of the mechanism of chemical reactions in the solid phase have both theoretical and practical importance, because many of the reactions used in industrial practice involve solid compounds. Thermal decomposition reactions occur in the metallurgical industry, in the production of catalysts, in the synthesis of new semiconductor materials and phosphors, in the preparation of ferrites, and in the decomposition of explosives. The solution of the problems presented by the control of all these processes is tightly bound up with an understanding of their mechanisms and their kinetics.

Even as recently as 10 years ago, very little attention was paid to the physical aspects of thermal decomposition reactions, but there is no longer any doubt that a sound understanding of the correlation between the kinetics and the electrophysical characteristics of decomposition reactions involving solid inorganic compounds is essential to further progress. The predominant role of ionic and electronic crystal defects in determining decomposition mechanisms and various electrophysical properties has been convincingly demonstrated[1,2]. Electrical conductivity, photoconductivity, contact phenomena, thermo-e.m.f., Hall voltage, and dielectric effects are among the electrophysical phenomena which have been most widely studied. A systematic appraisal of the electrophysical methods of investigation of thermal decomposition reactions, and an analysis of the results, are now needed.

2. STUDIES OF THERMAL DECOMPOSITION BY MEASUREMENTS OF ELECTRICAL CONDUCTIVITY

McDonald and Sandison[3] tried to determine the form of the nuclei of the new phase produced during the thermal decomposition of silver oxalate by combining measurements of electrical conductivity with kinetic studies of the decomposition reaction. For the case of two-dimensional (planar) nuclei, a sudden increase in electrical conductivity was expected when the nuclei began to coalesce (10–25% decomposition). However, the jump in conductivity was observed experimentally at 60% decomposition. The authors concluded[3] that three-dimensional (spherical) nuclei are formed in this reaction. Bel'kevich and Osinovik[4] repeated this work, and arrived at the opposite conclusion. Coalescence of the silver nuclei was observed at 17–30% decomposition of the silver oxalate, suggesting the formation of two-dimensional nuclei. Thus, entirely different results were obtained in nominally similar experiments. One possible explanation is that detailed differences in technique were responsible for the discrepancy, including sample preparation before pressing (drying, ageing, grinding), during pressing (temperature, pressure, duration), choice of electrode material and method of deposition, and, lastly, strength and frequency of the electric field used in the measurement and duration of the electrical stress applied to the sample. No special mention of these experimental details is made in the published papers[3,4], and therefore it is difficult to comment meaningfully. McDonald and Sandison did not describe their measurements of electrical conductivity. Bel'kevich and Osinovik's only comment is that electrical conductivity was measured with pressed samples, using a constant applied d.c. voltage of 1.3 V. The present writer has made a special study[5] of the influence of a d.c. electric field of 80 V cm^{-1} on the electrical conductivity and on the decomposition kinetics of pressed samples of silver oxalate. The field was applied continuously, or intermittently. Bel'kevich and Osinovik[4] have shown that the rate of decomposition of the sample goes through a maximum at the instant when the flash is observed: we have used this observation in our measurements. In the absence of an electric field the sample flashed at 143 ± 4°; with a periodically applied field (5 s, at 10 min intervals) the flash took place at 130 ± 2°, and when the field was applied continuously the sample flashed at 122°. In all cases, the extent of decomposition at the moment of the flash was the same, and a sudden increase in conductivity was observed. Hence it was concluded that a steady electric field accelerates the thermal decomposition of the oxalate, but has no effect on the shape of the silver nuclei. Savel'ev and Greben'[6] placed silver oxalate between condenser plates with a field of 6–10 kV cm^{-1}, and they also observed an accelerated vacuum thermolysis of the oxalate. Similar effects were found with silver and barium azide. The influence of a constant magnetic field (1100 Oe) on the decomposition of these compounds was also examined: both types of field were found to accelerate the thermal decomposition of

barium azide, and to lower the rate of decomposition of silver oxalate. Since transverse electric and magnetic fields can influence only electronic processes, it follows that these processes must play an important role in the thermolysis of barium azide and silver oxalate. These facts give valuable insight into the development of methods for studying electronic processes, and also into the nature of the electronic steps in the thermal decomposition of solids. Sviridov and Branitskii[7] showed that silver oxalate is readily decomposed by grinding: 35% decomposition of the oxalate can be achieved by grinding the material for 20 min. During this treatment the colour of the material changes from white, through grey, to black. We have noted a colour change in silver oxalate during cold pressing. Thus, the grinding and pressing operations used in the prepatation of the samples can lead to the mechanochemical decomposition of the oxalate, with formation of a solid product (colloidal silver) which acts as a catalyst during the subsequent thermal decomposition[8]. But what is the shape of the growing silver nuclei during thermolysis of the oxalate? Assuming that the shape of the silver nuclei is unaffected by the partial decomposition during pressing of the samples and by other artefacts during sample preparation and measurement of the electrical conductivity, and taking into account Griffith's observation[9] of a layered structure in the silver nuclei, Bel'kevich and Osinovik's hypothesis seems the more credible.

Garner and Heycock[10,11] monitored electrical conductivity in their study of the induction period attending the thermal decomposition of lithium aluminium hydride at 100°, and observed parallel changes in conductivity and in pressure of hydrogen evolved. The electrical conductivity increased by a factor of 2 (from 3×10^{-8} to 6×10^{-8} ohm^{-1}) in the first 35 min, reaching a maximum. After 45 min the conductivity had reverted to its original value, and after 160 min a minimum in conductivity was observed. After 500 min the conductivity rose sharply, as a result of the coalescence of the aluminium nuclei. The maximum and the minimum in electrical conductivity correspond roughly to points of inflection in the kinetic curves describing the thermolysis of the material. After the first point of inflection the rate of decomposition decreases by approximately 13%, and after the second point of inflection (corresponding to the conductivity minimum) the rate increases to a value 9% higher than the initial rate. Thus, a clear correlation exists between the rate of decomposition and the electrical conductivity of $LiAlH_4$. The authors showed that lithium aluminium hydride is a semiconductor, and suggested that its electrical conductivity at 100° is due to the presence of F'-centres. They further suggested that the formation and growth of aluminium nuclei proceeds by the association of F'-centres along dislocations and internal surfaces. The initial increase in conductivity is ascribed to an increase in the concentration of F'-centres (due to the desorption of hydrogen from the surface) and diffusion of the new F'-centres into the bulk, and the decrease in conductivity is identified with the association of F'-centres to give aluminium nuclei. This work provided one of the first unambiguous correlations between decomposition kinetics and changes in electrical conductivity.

Following the work of Garner and Heycock, Weidenthaler also reported a correlation[12,13] between conductivity and extent of decomposition as a result of his study of the thermolysis of silver oxide (in the form of pressed disks). The surface of the samples was found to be covered with a layer of Ag_2O_3, and the silver oxide behaved like an n-type semiconductor. Weidenthaler interpreted the proportionality between the extent of decomposition and the electrical conductivity of Ag_2O as evidence for the reaction

$$O^{2-} \rightarrow \square^{-} + 2\bar{e} + {}^1/_2O_2,$$

where $\square^-$ is an anion vacancy and $\bar{e}$ is a quasi-free electron.

However, other workers[14,15] found that silver oxide behaves like a typical p-type semiconductor. Garner and Reeves[16] measured the resistance of silver oxide samples undergoing thermolysis under "equilibrium" conditions (i.e. heated in an oxygen atmosphere), and observed a constant electrical conductivity and an activation energy (for the thermal decomposition of Ag_2O) approximately 6 times higher than Weidenthaler's value.

Torkar and coworkers[17,18] discussed the mechanism of thermal decomposition of silver azide in terms of their measurements of electrical conductivity. They observed a number of singularities in the temperature dependence of conductivity of silver azide samples heated at a uniform rate. The low-temperature electrical conductivity is ascribed to cation conduction by vacancies, and the high-temperature region (with a higher activation energy) to cation conduction by interstitials. In the high-temperature region sodium azide decomposes, and its electrical conductivity decreases because some of the interstitial ions are removed by the decomposition process. Further decomposition leads to an increase in conductivity, associated with the coalescence of the nuclei of the new phase. Under vacuum conditions the rise in conductivity is followed by full interlocking of the nuclei, and the electrical conductivity becomes independent of temperature over an appreciable temperature range. This stage is followed by flash decomposition. When the measurements are made in the air, the temperature coefficient of conductivity at first decreases, but eventually the activation energy adopts the same value as before the formation of nuclei, which is explained by the break-up of nuclei at the surface. These results were used to confirm the Mott mechanism of formation and growth of nuclei, involving alternate capture of electrons and interstitial cations. It would be interesting to devise an experiment to determine directly the nature of the current carriers. Conduction by vacancies can easily be distinguished from conduction by interstitials by the sign of the thermo-e.m.f., since these carriers stand in the same relationship as electrons and postive holes[19].

The writer has observed[20] anomalies in the temperature dependence of the electrical conductivity of silver sulphite, similar to the behaviour of silver azide. Above 156° the rate of thermal decomposition of silver sulphite begins to increase rapidly, and the electrical conductivity decreases and passes through a minimum. This effect is not observed[20,21] if the pressure used in the preparation of the samples is kept below 4 tonnes cm^{-2}, probably because conditions in low-density samples are not conducive to the development of ionic processes,[22] or because the partial mechanochemical decomposition of the sulphite does not take place at low pressures. The decrease in electrical conductivity was explained (as in the work of Torkar) by postulating association of interstitial cations, in keeping with currently held views on the mechanism of thermal decomposition of silver sulphite[23]. The sign of the thermo-e.m.f. confirms that interstitial cations are responsible for the fall in conductivity; the lack of dependence of the effect on the composition of the atmosphere leads to the same conclusion.

In ammonium perchlorate, heated in the temperature range 230–270°C, the rate of thermal decomposition[24] goes through a maximum (238°) and a minimum (251°). We find[25] that the thermal conductivity of the perchlorate (in contrast to that of silver sulphite) varies in the same sense as the rate of decomposition. This is evidently due to the generation of intrinsic current carriers during the decomposition of the perchlorate. Adopting Boldyrev's interpretation[26] of the initial stages of the thermolysis of ammonium perchlorate, and taking electrophysical data into account[25], it is easy to account for these anomalies. The native current carriers in ammonium perchlorate must be proton vacancies, since their concentration increases during decomposition of the perchlorate.

Zhuravlev and coworkers[27] studied the decomposition of silver oxalate, and observed a minimum and a maximum in electrical conductivity 60 and 120 min respectively after the crystals had been heated to the decomposition temperature. Conductivity was measured on crystals $2 \times 0.1 \times 0.1$ mm^3 in dimensions by a contactless method. The fall in conductivity during the initial stages of decomposition was ascribed to the loss of weakly held interstitial cations, with formation of silver nuclei. A special study of the desorption of water molecules in relation to this effect showed that desorption of water does occur, but its contribution to the loss of electrical conductivity by a factor of 6 during the early stages of decomposition is far from predominant. The subsequent increase in conductivity is due to the accumulation of metallic product. Although the authors did not specifically attempt to investigate the mechanism of thermal decomposition, their experimental methods are undoubtedly interesting.

Young[22] studied the electrophysical properties of silver azide before and during decomposition, and concluded that the best method for studying the sintering of solids is to measure electrical conductivity with a d.c. applied potential, using powdered samples held between metallised glass plates. Detonation of the silver azide was observed in d.c. fields in excess of 250 V cm^{-1}. Young stresses the importance of the method of sample preparation and of the rate of heating and cooling in controlling the reproducibility of conductivity measurements. However, we cannot accept his conclusion that ionic conduction is more developed in the denser samples. Thus, Gladkovskii and Meiklyar[28] concluded from their electrical measurements that single crystals of silver bromide are electronic semiconductors, whereas polycrystalline samples show mainly ionic conductivity. Andrievskii and coworkers[29] observed faster diffusion of various ions (in isotopic form) in polycrystalline cuprous oxide than in single crystals of the same oxide. The conditions which favour the ionic or the electronic component of the conductivity are probably best discussed in the light of the structural and defect parameters of the samples.

It has been shown[30–36] that potassium permanganate and its solid decomposition products are electronic semiconductors, and the elementary mechanism of the thermolysis of this compound has been discussed[37]. The formation of potassium manganate (one of the decomposition products) in solid solution raises the conductivity of potassium permanganate in the structure-sensitive region and lowers the activation energy for conduction. Similar effects were observed in measurements of the conductivity of partly decomposed samples. It was concluded that the manganate formed by thermal decomposition of potassium permanganate is initially present in solid solution, in agreement with the report[38] that the crystal lattices of potassium manganate and permanganate are isomorphous, and with Glemser and Buthenuth's work on the decomposition of potassium permanganate in the beam of an electron microscope.[39] The writer has pointed out[36] that the β and γ modifications of manganese dioxide can be distinguished by the temperature dependence of their electrical conductivity, and hence that the manganese dioxide obtained as the end product of the thermal decomposition of potassium permanganate is not in the β modification. These results have shed new light on the differences of opinion[40–43] regarding the catalytic effect of manganese dioxide on the thermolysis of potassium permanganate: the discrepancies were due to failure to take account of the crystalline modification of the dioxide.

The method of homo-phase additives is widely used in studies of the influence of microdefects on the thermal decomposition of ionic salts. By artificially varying the concentration of a given kind of point defects in a crystal—usually Schottky or Frenkel' defects—the role of various defects in the thermal decomposition of the crystal can be clarified and suggested intermediate steps can be confirmed. Furthermore, the homo-phase additive method gives an indication of the presence of ions of different valency in the lattice of a solid electrolyte. Measurements of electrical conductivity are most commonly used for this purpose, since they offer a quick and simple test for substitutional solid solutions. When solid solutions are formed, the plot of electrical conductivity against concentration of additive has a characteristic V-shape[44–48]. The method enables the ionic defects which act as the main charge carriers to be identified (cations, anions, cation vacancies, anion vacancies), and it allows their concentration and mobility to be calculated by the Koch–Wagner method[49,50]. However, the homo-phase additive method has also a number of shortcomings. As a rule, only the change in concentration of ionic defects is considered, even though several other changes may occur in the crystal at the same time. The additive can affect the mobility of the ionic defects, the lattice parameters, and the concentration of electronic defects. High concentrations of additives can deform the crystal, thus perturbing the crystal field, and generating localised stresses in the crystal which can influence the electronic steps in the thermal decomposition reaction. Radically different conclusions can result if all the relevant factors are taken into consideration in the discussion of the effect of additives on the rate of a solid-phase reaction[47]: hence, it is important to give due weight to all such factors. The problem is by no means new. For example, lattice deformation and a change in the lattice parameters of silver oxalate were detected by X-ray diffraction[46] when bivalent lead ions were added in concentrations above 1 mol.%. Solov'eva and coworkers[51] stressed the need to allow for the effect of impurities on the mobility of ionic defects in studies of solid-state reactions. Brenet[52] observed that either the β or the γ modification of manganese dioxide can be obtained as the decomposition product of manganese nitrate by adding different homo-phase impurities, and that these modifications have different catalytic properties[53]. Lastly, a common weakness of many investigations by the method of additives is the lack of firm evidence on the amount of impurity which has entered the lattice. In this respect, the recent application of ESR by Boldyrev and coworkers[47,54] to the quantitative determination of impurity in the lattice is noteworthy.

Thus, relatively few papers have been published on the rational application of electrical conductivity measurements to the study of thermal decomposition mechanisms in solids, but the results obtained so far offer conclusive

evidence that these measurements give valuable information when interpreted in the light of recent advances in solid-state physics. Thus, the further application, development, and refinement of these methods is to be welcomed.

3. USE OF PHOTOCONDUCTIVITY PHENOMENA

Maclaren and Rogers[55] observed photoconductivity in the region of the long-wave intrinsic absorption edge of undecomposed silver azide. With a partially decomposed sample the photoconductivity maximum is shifted towards longer waves, as a result of the photoeffect in the silver nuclei. The authors concluded, from the existence of photoconductivity at the decomposition temperatures of silver and lead azides, that the first decomposition step consists in the transfer of an electron to the conduction band, followed by trapping of the electron at an interstitial cation: the latter condition is favourable to the decomposition of the N_3 radical. These results suggest the possibility of applying photoconductivity measurements to the study of the nucleation of metals in azides, and to the interpretation of the autocatalytic effect of the solid decomposition product in azides. The catalytic effect of electron-acceptor impurities, predicted by this mechanism, was demonstrated by Mitchell.[56] Young's more careful measurements showed[22] that photoconductivity is absent in freshly prepared silver azide, and becomes significant only after partial decomposition of the material. This worker suggested that all the specimens used by Maclaren were partly decomposed by irradiation or by spontaneous ageing.

Forty and coworkers[57] studied nucleation in lead iodide undergoing thermal decomposition from the accompanying photoconductivity changes. The photoconductivity decreases as soon as lead nuclei appear: this effect is ascribed to the acceptor properties of the nuclei. The nucleation of lead in lead iodide is very fast at 180° because of the ready association of F-centres at this temperature, with trapping of free electrons. However, the nucleation of a new phase and loss of photoconductivity may result, also, from free electron trapping at interstitial cations. Dedman and Lewis[58] studied photoconductivity in lead azide with the aim of correlating the electrophysical properties and the decomposition kinetics of the compounds. Measurements of dark conductivity and photoconductivity in polycrystalline and single-crystal samples of lead azide gave different results. Heat treatment increased both the dark conductivity and the photoconductivity of the material, possibly as a result of incipient decomposition. The photocurrent was ascribed to exciton dissociation with formation of free electrons and positive holes. The dissociation energy of the excitons was calculated from the temperature dependence of the photoconductivity. The increased photoconduction in partially decomposed crystals was explained by postulating an increase in the mobility of the electrons.

Boldyrev and Skorik[59] studied the gamma- and photoconductivity of silver and barium azides under thermal decomposition conditions. In the decomposition of barium azide the electrical conductivity was significantly increased by irradiation with X-rays (using a dose rate of 110 rad min^{-1}). In the thermal decomposition of silver azide neither gamma- nor photoconduction was observed. The authors suggest that the decomposition of barium and silver azides proceeds through the formation of free electrons followed by electron capture at interstitial cations, and they conclude that the rate of thermal decomposition of the azides should be proportional to the concentration of free electrons as long as this concentrarion is smaller than the concentration of electron traps. It is suggested that this condition obtains in barium azide, since its rate of decomposition increases during irradiation with X-rays. The rate-limiting step in the thermal decomposition of barium azide is thought to be, on the basis of the above results, the transfer of an electron from an anion to the conduction band. In silver azide, on the other hand, the rate of thermolysis is unaffected by irradiation. It follows that the excitation of electrons to the conduction band is not rate-limiting in the decomposition of silver azide, in spite of statements to the contrary[49,55].

Zakharov and Savel'ev[23,49] concluded, from the absence of photoconductivity in pressed samples of silver sulphite and oxalate, that the thermal decomposition of these compounds involves the excitation of electrons from the valence band to exciton levels, and not to the conduction band. The absence of photoconductivity was used as an argument for classifying silver sulphite and oxalate among ionic conductors. Photoconductivity (like the Hall effect[60]) is one of the most accurate and unambiguous methods for the detection of electronic conduction in ionic compounds, but even when these effects are vanishingly small it cannot be argued that significant (or even predominant) electron or hole conduction must be absent[61]. This situation may arise through the dependence of the photoconductivity and the Hall e.m.f. on the mobility of the charge carriers: thus, the method is severely restricted by the limitations of the existing apparatus and experimental techniques for measuring these characteristics. It has been shown[62] that the Hall e.m.f. becomes very difficult to measure when the electron (or hole) mobility is lower than 0.04 $cm^2 V^{-1} s^{-1}$. Photoconductivity is difficult to measure[63] in semiconductors with a carrier lifetime below 10^{-4} s. Thus, arguments on the exciton mechanism of the initial stages of thermal decomposition of solids should be accepted with caution if they are based solely on the absence of photoconductivity or Hall effect.

4. APPLICATION OF ELECTROPHYSICAL PHENOMENA AT THE BOUNDARY BETWEEN TWO SOLIDS

Electronic effects[64-66] at the interface between two solids have been used with success[67-73] to discuss catalytic and autocatalytic mechanisms in the thermal decomposition of ionic salts. Because of differences in work function between the host material and impurities, the region of the crystals adjacent to the contact may become enriched or depleted in electrons. According to recent views[1,2,74], the thermal decomposition of ionic salts involves both electronic and ionic steps. Any change in concentration of the free electrons in the reaction zone can affect (directly or indirectly) the rate of thermal decomposition of the material[68,75]. Electrons near the contact always tend to pass into the medium with the higher work function. By suitable choice of dopants, this effect can be used to bring about a redistribution of the electron density near the surface in the desired sense. The effectiveness of catalytically active impurities is determined by the thickness of the depleted layer, which is proportional to the contact potential difference.

Contact phenomena were first invoked by Erofeev[67] to explain the mechanism of thermal decomposition. As the contact potential difference between an ionic compound

and the metal increases, the number of anions in the surface layer increases, and so does also the rate of thermal decomposition of the material. Using this approach, Erofeev postulated a proportionality between the rate of decomposition and the work function of the solid product of the reaction (for the case of solids with a common anion and cations of similar electronic structure). He quotes as an example the azides of barium, strontium, and calcium, in which the activation energy of thermal decomposition is found to be inversely proportional to the work function of the corresponding metals (which are also the decomposition products of the azides).

The realisation of the important role played by contact potential in thermal decomposition reactions has already produced useful results, but in many cases the available data are not sufficiently reliable. Thus, it is difficult to compare the electronic work functions of barium, strontium, and calcium[67] from results obtained under different conditions and by different methods because the scatter of the data is excessive. Fomenko[76], by averaging the results of 10–18 investigations, concludes that the work function of strontium is lower than that of barium. Thus, there is little justification for the statement that the rates of decomposition of barium, strontium, and calcium azides vary in the same sense as the work functions of the corresponding metals. Equally unjustified is the assumption that azides with different crystal lattices[77] and different physical properties[2,56] can have the same work function simply because they have a common anion and cations from the same group of the Periodic Table. To prove Erofeev's hypothesis we require a knowledge of the relative work functions of the contacting pairs of materials under the conditions which apply during the thermal decomposition of the azides: in particular, suitable allowance has to be made for the influence of a number of factors on the work function of metals and ionic crystals.

The method most commonly used to determine the thermodynamic work function is the vibrating condenser method[78–81], in which the key element is a vibrating metal plate whose work function is taken as standard. Allowance must be made for any change in the work function of the standard metal under the conditions used in the thermal decomposition of the experimental material. The electronic work function of metals usually decreases with increase of temperature[82,83] (if other complicating factors are excluded), and depends on the nature of any adsorbed gas[76,84,85]. The work function of compounds is even more sensitive to temperature[76,86,87], composition of the atmosphere[76,88–91], state of the surface, and intensity of illumination[92–94]. The electronic work function is a surface electronic characteristic of solids[95,96]. It is determined by the properties of a few monolayers of the material, since the surface of a crystal can be defined[97] as a layer of thickness equal to the mean free path of electrons, and therefore proportional[98] to the electron mobility and effective mass. Hence, the work function is affected by surface contamination (whether accidental of deliberate), and by the lapping and polishing treatments applied to the surface. If the decomposition product is a metal, we must allow also for the geometric factor[99,100] (an increase in work function with decreasing particle size). For example, Sviridov and Branitskii[8] found that the autocatalytic effect of silver nuclei in the thermolysis of silver oxalate disappears when the nuclei reach a certain critical size: one explanation of this effect could be the influence of the geometric factor.

Zakharov and Savel'ev[68,69] analysed published data on the effect of various oxides on the rate of thermolysis of potassium permanganate, ammonium perchlorate, and potassium chlorate, and noted a clear correlation between the catalytic effect of the oxides and their work function. Oxides with the highest work function had the strongest catalytic effect on the thermolysis of all three compounds. The thermal decomposition of silver oxalate was found[68] to be accelerated by additions of nickel oxide or cuprous oxide. On the other hand, zinc oxide or silver sulphide additions inhibit the decomposition of silver oxalate. In these experiments, too, the catalytic effect of the oxides was proportional to their work function, even when the work function values used in the calculation had been obtained under conditions far removed from those of the decomposition reaction. In a more recent paper[70], Zakharov and coworkers quote their own measurements of work function for silver azide and various additives under conditions close to those used in the thermal decomposition of silver azide. A more exact proportionality between the catalytic effect and the work function of the additives was observed, in spite of the failure to allow for oxygen evolution from the oxides at the decomposition temperature of the azide, and for the effect of the evolved oxygen on the work function of the standard gold electrode. A similar experiment is needed also to characterise the effect of the nitrogen (evolved from the silver azide) on the work function of the additives and of the standard. The experiment could take the form of a measurement of the contact potential difference between two gold plates under conditions leading to the decomposition of the appropriate substances.

Boldyrev and coworkers[71] confirmed the presence of electron-acceptor autocatalysis by manganese dioxide in potassium permanganate by measuring the work function of both materials at room temperature in an atmosphere of air, using the vibrating condenser method. The electronic work function of manganese dioxide was found to be 5.48 eV, that of potassium permanganate 4.76 eV. Hence, electron-acceptor catalysis is a possibility.

However, a number of criticisms must be levelled at this work, if only in order to highlight the complexity of the problem. The direction of electron transfer at the $KMnO_4$–MnO_2 boundary was determined from work function measurements made under conditions far from those which exist during the decomposition of potassium permanganate. Furthermore, the form of the manganese dioxide used in these experiments is not stated: the compound can exist in two stable modifications[101,102] as well as in an amorphous form. It is known[64–66] that the electronic work function of a semiconductor is equal to the sum of the work done against the electrical image forces and one-half of the width of the forbidden gap. Assuming that the work done against the electrical image forces remains the same for crystalline and amorphous forms of a compound as long as the short-range order is preserved[74,103–105], the work function difference between the two forms can be estimated from the difference in the forbidden gap. The γ modification of manganese dioxide has a greater activation energy for electrical conduction than the β modification.[53] Hence, we can expect the work function of γ-MnO_2 to be greater than that of β-MnO_2. When a compound is converted into the amorphous state the width of the forbidden gap usually increases because of the decrease in density[64,106]. For example, iodine (which is known to be a semiconductor[107]) has a work function of 2.8 eV in the monoclinic form and 6.8 eV in the amorphous state.[76] Hence, the most marked effects on the thermal decomposition of the original solid will be observed when the decomposition product (or the additive) is in the amorphous state if the catalysis is of the electron-

acceptor type. However, the production of manganese dioxide in an amorphous state during the thermolysis of potassium permanganate is highly unlikely[41].

In addition to the contact potential difference measured by the vibrating condenser method, the contact resistance can be used to compare the work functions of semiconductors, since it is associated[64-66] with the contact p.d. of the metal–semiconductor pair. The contact resistance is measured by the exponential portion of the current–voltage characteristic of the pair. By using different metal electrodes it is possible to evaluate[108] the work function of a semiconductor of a given conductivity type. The writer has used this method[73] to study the thermal decomposition of silver permanganate at 115°, catalysed by metal oxides. ZnO and ThO_2 were found to accelerate the thermolysis of silver permanganate, Co_3O_4 and NiO had no effect, and TiO_2 inhibited the process. No definite correlation was observed between the catalytic activity of the oxides and their published work functions. To explain the results, an electron exchange process between the additive and the undecomposed material through a layer of products was postulated. The current–voltage characteristics obtained at a number of temperatures for ZnO, $AgMnO_4$, and its solid decomposition product against platinum and gold electrodes were used to give a comparative assessment of the work functions of all these materials. The work function of zinc oxide was found to increase with temperature, whereas the work function of the decomposition products decreased and that of silver permanganate showed a barely significant increase. It was concluded from these results that under the conditions leading to decomposition of silver permanganate the electrons in the ZnO–product–$AgMnO_4$ system are transferred from the decomposition product towards both the zinc oxide and the silver permanganate. Mechanical admixture of the decomposition product or of its separate components (manganese dioxide and silver oxide) was found to inhibit the thermolysis of silver permanganate very markedly. Electron transfer from the decomposition product to the zinc oxide appears to minimise the inhibiting effect of the former and to accelerate the decomposition of the permanganate.

All the authors whose work has been discussed so far have considered only one effect at the contact: the transfer of electrons towards the material with the highest work function. This is by no means the only manifestation of contact phenomena at the solid–solid interface in catalysis and autocatalysis. Firstly, no account had been taken of the possible effect of the electric field at the contact. For the electrical conductivities and work functions of the materials most commonly investigated in solid-state chemistry, the voltage drop across the electron-deficient ("depletion") layer at the interface is of the order of 1 volt. Assuming a normal electron mobility and effective mass for ionic crystals, the thickness of the contact layer works out[98] to 10^{-4}–10^{-6} cm. Thus, the contact region of materials undergoing decomposition may experience electric fields of the order of 10^4–10^6 V cm^{-1}, i.e. field intensities sufficient to bring about decomposition. Furthermore, contact electric fields and electron transfer phenomena may occur not only at the contact between two different substances but also at the contact between crystals of the same material. The effect may arise from work function differences between different crystal faces: it has been observed in crystals of metals[76] (manganese, copper, silver, tungsten) and of semiconductors. The difference in work function between different faces in cadmium and lead sulphides[94] lies in the range 0.1 to 0.3 eV. Assuming an average depletion layer thickness of 10^{-5} cm, we obtain a contact surface field of the order of 10^4 V cm^{-1}. We cannot exclude the possibility that this effect may influence the rate of thermolysis of solids; the effect may also be responsible for the maximum observed in the plot of rate of thermolysis against degree of dispersion for a number of substances[109,110].

5. POTENTIAL APPLICATIONS OF THERMO-E.M.F. AND HALL VOLTAGE PHENOMENA

Although the well known thermo-e.m.f. phenomena can be measured simply[25,78,107,111] and without costly and cumbersome apparatus, it has not so far been used to any significant extent in studies of the mechanism of solid-state reactions. Even a cursory study of published work on the thermo-e.m.f. of ionic crystals reveals a number of questions of great importance to solid-state chemistry[1,2,74] and which could in principle be answered by measurements of thermo-e.m.f.

The existence of solid solutions in crystals can be recognised from anomalies in the differential thermo-e.m.f. isotherms[112-114]. Electron conduction in semiconductors can be distinguished from hole conduction by the sign of the thermo-e.m.f., even when alternative methods fail, as in polaron semiconductors[61,115,116] (oxides with partly filled 3*d* shells). In solid electrolytes, ionic conduction by interstitials can be distinguished from ionic conduction by vacancies according to the sign of the thermo-e.m.f. The differential thermo-e.m.f. (or thermoelectric power) in solid electrolytes can be used to calculate[44,117] the activation energy attending the formation and the motion of ionic defects. The concentration of current carriers in semiconductors of the band[118] and the polaron[119] types can be calculated from the thermo-e.m.f., and changes in carrier concentration due to various effects can be monitored.

The thermo-e.m.f. has one important "drawback" in comparison with the Hall effect, the photo-e.m.f., and photoconductivity. The former can be induced by charge carriers of any kind, whereas the latter three effects are specific to electronic and positive hole process. However, the ionic thermo-e.m.f. becomes significant only at high temperatures (most commonly, in the region of intrinsic ionic conduction), because ionic mobilities are extremely low. Under these conditions the concentration of ions involved in the conduction process, and their mobility, become high enough to support a significant thermoelectric current. However, with mixed (electronic–ionic) conductors, or when the conduction type is unknown, the characteristics of both ions and electrons can be calculated by combining the measurements of thermo-e.m.f. with other methods of measuring the kinetic parameters of charge carriers (Hall voltage, transport numbers, photo-e.m.f., and photoconductivity). Very little has been published[44,117,120] on the ionic thermo-e.m.f.: the phenomenon is much less well documented than the electron (or hole) thermo-e.m.f. But even among the few available results, some are difficult to accept (particularly those relating to thermionic currents). For example, the report by Reingold[120] of an ionic thermo-e.m.f. in silver sulphide, selenide, and telluride is unconvincing since these compounds are known to be electronic semiconductors[19,61,121,122]. However, in spite of the rare occurrence of ionic thermo-e.m.f.s, the contribution of ions to the total thermo-e.m.f. should always be treated as a possibility.

There is little published information on the thermo-e.m.f. (or other electrophysical properties) of the complex systems of interest in studies of solid-state reactions. The early work of Lashof[123] on the electrophysical properties of lead chromate is noteworthy. In spite of the low conductivity of lead chromate (of the order of 10^{-9} ohm^{-1} cm^{-1} at 100°), measurements of transport numbers and of thermo-e.m.f. showed that the compound is an electronic semiconductor. Lashof was among the first to point out the importance of colloidal metal particles (formed by thermal or photochemical decomposition) in the development of electronic conduction in ionic salts. The Hall effect of lead chromate could not be measured because of the high resistance of the samples. The sign of the thermo-e.m.f. was taken as evidence that the conductivity is by electrons (and not by holes). Good agreement was obtained between the measured thermo-e.m.f. and the value calculated from the free electron model: this was quoted as additional evidence that $PbCrO_4$ is an n-type semiconductor. Lashof's work is interesting for the methods used, but it failed to characterise satisfactorily the mechanism of electronic conduction, since the author[123] ignored the possibility of electron transfer between chromium ions of different valencies, which is frequently found in systems of this type[124-127] and accounts for most of their electronic conduction.

The writer[20] has used the thermo-e.m.f. to demonstrate cation transport through interstitials of the silver sulphite lattice, and hence to confirm the growth of nuclei by the Mott mechanism. The sign of the thermo-e.m.f. was one of the arguments[25] in favour of a proton conduction mechanism through vacancies in the cation sublattice of ammonium perchlorate, in agreement with the onset of thermal decomposition[26]. Measurements of thermo-e.m.f. have been used[31,36,73] to confirm the n-type conduction of univalent metal permanganates, in which photoconductivity and Hall effect could not be measured.

Young[2,22] applied the thermo-e.m.f. phenomenon in his studies of electronic and ionic processes in pure and in partially decomposed silver azide. By combining these measurements with optical spectra, Hall e.m.f., electrical conductivity, and photoconductivity studies he concluded that undecomposed silver azide is a cation conductor, whereas the same compound partly decomposed by heating or illumination is an electronic conductor. He suggested that the optimum conditions for electronic conduction occur in powdered samples, and the optimum conditions for ionic conduction occur in monolithic samples. Colloidal silver particles, formed during irradiation or heating, are responsible for the electronic conduction of these samples.

Young[22] quotes his measurements of thermo-e.m.f. in support of these conclusions. The differential thermo-e.m.f. of partially decomposed (up to 180°) silver azide remains negative but decreases in absolute value. Beyond this temperature the coefficient changes sign, reaching a maximum at 185°, and at 187° it falls almost vertically, changes sign, and goes through a sharp peak at 190°. At 192–193° the thermo-e.m.f. of the azide decreases very rapidly, changes sign, and returns to the previous maximum value. The final value remains unchanged on cooling the sample. This complicated and unusual variation of thermo-e.m.f. with temperature is consistent with the conclusions reached by Young from his measurements of the other electrophysical properties of the material. The first change of sign of the thermo-e.m.f. is due to sintering of the particles, and "displacement" of electronic conduction by cationic conduction. The anomalies in the region of the transition at 190° are explained by alternate enhancement and interaction of electronic and cationic conduction as a result of the collapse and re-growth of crystals during heat treatment. According to both electrical conductivity and thermo-e.m.f. measurements, this transition in silver azide is irreversible. However, the temperature difference used by Young (2–3°) may have been too low[118] to give reliable values of the differential thermo-e.m.f.: a temperature difference of the order of 10° across the sample is preferred[128,129] for the measurement of differential thermo-e.m.f.

The Hall e.m.f. is a reliable method[60,61,64] for separating the electronic component of the conductivity and at the same time determining the concentration of the charge carriers. The method can be used to monitor changes in the concentration of free electrons and holes during various types of treatment of solids (including decomposition). However, the sensitivity of existing apparatus is inadequate to identify the mechanism of solid-state reactions in the majority of solid inorganic compounds. So far, the Hall effect has been used to study electronic processes in solids having a resistivity not greater than 10^8 ohm[130-132]. A more promising method of studying reactions in solids is the photo-Hall effect[133-136], in which the Hall e.m.f. is generated by light-induced electrons, since many of the compounds used in research on solid-state reactions are ionic conductors[1,2]. For example, in silver azide the Hall e.m.f. appears only after partial decomposition[22], showing that the undecomposed azide is an ionic conductor and confirming Young's hypothesis on the donor properties of colloidal silver particles.

6. USE OF DIELECTRIC CHARACTERISTICS

The dielectric constant and the tangent of the dielectric loss angle are the most important electrophysical characteristics of a material. The variation of these characteristics with temperature, frequency, atmosphere composition, illumination, and pre-treatment (heating, irradiation, grinding, etc.) gives valuable information[64,137-143] on the mechanism of thermal decomposition of solids. The variation of ϵ and $\tan\delta$ with frequency reflects changes in physicochemical properties such as mobility and concentration of charge carriers, decomposition of neutral associations of ionic defects, effective mass of electrons and holes, and phase transitions[144-146], which may accompany the thermal decomposition of ionic salts. The rate of thermal decomposition usually changes rapidly at temperatures close to the modification transition[20,21,24,25], and so does also the electrical conductivity. Measurements of ϵ and $\tan\delta$ can be expected to give additional information on changes affecting electronic and ionic processes in the temperature region of the modification transition.

Very little has been published on the application of ϵ and $\tan\delta$ measurements specifically to the study of reaction mechanisms in the solid state. This is due, at least in part, to the experimental difficulties and to the difficulty of interpreting the results. In addition to the detection of modification transitions, two applications of ϵ and $\tan\delta$ in solid-state chemistry should be mentioned. They are the detection of solid solution formation from dielectric characteristics[45,46,147] and the calculation of the activation energy of thermally excited electrons[2,55-58] from the dielectric constant and the optical excitation energy of the electrons to the conduction band. The well known Mott formula[148] is used in the latter calculation. Having determined the width of the forbidden gap, and converted the optical

excitation energy into the thermal excitation energy by the Mott formula, this latter value is compared with the experimentally observed activation energy of the thermolysis reaction. Close agreement between theory and experiment is taken as evidence that electronic excitation is the rate-limiting step of the thermolysis reaction. However, Mott's formula is known to be only an approximation in calculations of this type.[75] A number of experimental findings are inconsistent with Mott's formula[61,107,148-152]. Alkali-metal halides with *F*-centres, barium and zinc oxides, and zinc and cadmium sulphides are semiconductors for which the activation energy differs very substantially from the expected value. Alkali halide crystals become semiconductors when colour centres are induced in them. By analogy with Sikorskii's results[153] for sodium chloride, the influence of *F*-centre polarisation on the static dielectric constant can be ignored. Thus, energy calculations by Mott's formula can be misleading.

Suzuki and Kotera[154] studied the kinetics of the anatase–rutile phase transformation by a dielectric method. The ϵ values of these modifications of titanium dioxide differ by a factor of 3.5. Hence, the presence of a new phase could be detected by the dielectric method even at concentrations below 10%. The method is particularly attractive, since the variation of ϵ with the concentration of the new phase is almost linear.

Ellis and Hall[155] used the dielectric method to monitor changes in the defect structure of sodium azide during thermal decomposition. The decomposition kinetics were studied, in parallel with ϵ and $\tan\delta$, from the pressure changes in the vacuum system. No change of ϵ was noted during the early stages of decomposition, but both ϵ and $\tan\delta$ showed a sharp maximum near the point of inflection in the decomposition curve. With further decomposition, the low-frequency values of ϵ and $\tan\delta$ continued to increase, whereas the high-frequency values did not change significantly. The authors ascribe these changes in the dielectric characteristics to the lattice defects produced during decomposition, rather than to the decomposition products. Since the predominant ionic defects in sodium azide are believed to be of the Schottky type, defect pairs consisting of an *F*-centre and an anion vacancy are likely to be formed during thermolysis. The *F*-centres may be formed by the reaction

$$2N_3^- \rightarrow 3N_2 + 2\bar{e} .$$

Zhuravlev[156] made a detailed study of the dielectric properties of silver oxalate and silver nitrite before and during thermolysis. The dielectric properties before decomposition had to be studied in order to establish the nature of the dielectric losses and of the polarisation. It was concluded that electrical polarisation in these compounds consists mainly of electronic, ionic, and migrational polarisation, and these processes were invoked in the discussion of the decomposition mechanism. A sharp decrease in $\tan\delta$ and in electrical conductivity was noted[156] during the early stages of the thermal decomposition of silver oxalate and nitrite. It was shown that the reaction kinetics during this period can be followed from the changes in $\tan\delta$, and that the rate of disappearance of defect ions (with formation of a metallic phase) can be assessed in the same way. The dielectric constant does not change at first, but after some time it begins to rise very rapidly, suggesting the coalescence of fine silver nuclei into coarser structures. The overall conclusion was that the decomposition kinetics of compounds of this type can be studied by using changes in dielectric properties to monitor the amount of metallic phase produced.

Thus, a comprehensive and objective study of electrophysical properties is a powerful means of characterising the electronic and the ionic steps in the thermal decomposition of solids.

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Present State of the Oscillopolarographic Method of Analysis

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This review considers the main achievements of oscillographic polarography with a given form of polarisation voltage. Methods for increasing the sensitivity and resolving power of this analytical method and its use as a method for studying the mechanism of electrochemical processes are discussed. The influence of various factors determined by the composition of the solution in the cell and by the nature of the substances being studied on the form of the oscillopolarographic curves, and the characteristic features of the use of the method in the analysis of inorganic and organic compounds are examined. The bibliography contains 238 references.

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I. INTRODUCTION

Recent years have been characterised by further development of the oscillopolarographic method of analysis. A number of new papers have been published, in which considerable attention has been paid to the theory of the method and to its various practical applications; papers demonstrating the advantages of oscillopolarography as a highly sensitive method of analysis over other electrochemical methods have been published. Oscillographic polarography is at present used in organic, bio-organic[1], analytical, and physical chemistry, pharmacology and medicine, clinical studies and therapy, geochemistry, oceanography, and botany. Thus the materials studied include not only synthetic laboratory mixtures, but also natural materials such as minerals, petroleum, living tissue, plant materials, etc.

Recently, however, the accepted description of the method as "oscillographic polarography" has often been replaced in non-Soviet literature by other descriptions; this introduces certain difficulties, and sometimes even confusion. To standardise terminology and facilitate the classification of electrochemical (particularly polarographic) methods, and to permit generalisation of the results of studies by different workers using essentially the same method under different descriptions, the term "oscillographic polarography" should be preserved, although it may be noted that this description does not fully reflect the essential features of the method. In this method, in which the rapid change in the electrode potential brings about a rapid change in current strength, the polarisation curves are recorded with an inertia-free instrument—a cathode-ray oscillograph; hence the name of the method. The oscillograph, however, is also used, together with a string galvanometer, to record the current–time curves at constant potential, and also to record curves in chronopotentiometry[2] and other relaxation electrochemical methods[3] used to study the kinetics and mechanism of electrode processes. On the other hand, in oscillographic polarographs the rate of increase in potential can be varied within certain limits, and it can be made relatively small, comparable with the rate in classical polarography. Thus there is no sharp distinction between these methods[1,4].

The present state of oscillographic polarography is characterised by considerable variety in the versions of the method and the associated techniques of oscillopolarographic measurement[5-9]. These versions are classified according to four familiar features[6], of which the chief is the form of the polarising voltage. The latter determines to a considerable extent the electrical circuit and the oscillopolarographic assembly. Depending on the form of polarising voltage, it is possible to distinguish methods involving a linear polarising pulse—saw-tooth, symmetrical triangular, etc.—and methods involving a potential which changes non-linearly, for example according to a sinusoidal law.

The method involving the recording of the plot of $I = f(E)$ with a linearly changing voltage is called Randles–Sevcik oscillographic polarography; other names encountered in the literature are: voltammetry with continuously changing potential, voltammetry with change in potential or with scanning of the potential, and chrono-amperometry with scanning of the potential (particularly in the American literature[9]). Another method of oscillographic polarography—with a given sinusoidal current[7]—makes it possible to obtain oscillopolarograms in the form of the plots of dE/dt against E (these curves give the dependence of the rate of change of potential at the polarised electrode on its potential).

The method involving the recording of the $dE/dt = f(E)$ curves has been developed chiefly by the Prague school of polarographers. Regular symposia on oscillopolarography, and special courses for the training of specialists have helped the development and extensive application of this method of analysis in Europe[10-12], and papers have recently been published by South American workers[13]. The method involving the recording of $I = f(E)$ curves has also developed considerably in recent years, and there has been a marked increase in the volume of factual material obtained by this method.

In the Soviet Union this has been assisted by the mass production of the Soviet OP-1-61 oscillopolarograph and more particularly the PO-5122 01-02 and 02A oscillopolarographs.

The fact that recent work has not been reviewed makes it somewhat difficult to evaluate the main achievements of oscillographic polarography. In the present

review an attempt is made to fill this gap and to give a picture of the present state of this physicochemical method of analysis.

Most attention has been paid to the method involving the recording of $I = f(E)$ curves, since the other method mentioned above has been dealt with fairly fully in an earlier review[1]. Where necessary for comparison, however, data from papers dealing with the method involving the recording of $dE/dt = f(E)$ curves are introduced.

II. SOME THEORETICAL ASPECTS OF THE STATE OF THE OSCILLOPOLAROGRAPHIC METHOD OF ANALYSIS

1. Sensitivity and Resolving Power, and Methods for Increasing Them

The analytical applicability of classical and oscillographic polarography is usually estimated on the basis of the sensitivity and resolving power of the method. The sensitivity is characterised by the magnitude of the minimum concentration which can be reliably determined from the oscillopolarogram, and the resolving power is determined by the possibility of carrying out the simultaneous polarographic study of two substances. Resolving power with respect to potentials and resolving power with respect to concentrations are distinguished. If a single polarographic cell is used for the polarographic study, that is if the difference method, discussed below, is not used, and if the method involving build-up at the electrode is not used, the minimal concentration of a substance, undergoing reversible reduction, which can be determined in the solution is 5×10^{-7} M [4], with a resolving power with respect to potentials equal to ~40 mV [14] (for a polarising voltage of linear form).

The chief factor limiting the sensitivity of modern oscillographic polarographs is the capacity current. The total current for electrolytic reduction, recorded by the oscillograph, consists of the Faraday current I_e of the electrochemical reaction, associated with the transfer of electrons, and the capacity current I_c, which appears as a consequence of the existence of the electrical double layer. The sensitivity of the oscillopolarographic method is determined not by the magnitude of the total current but by the ratio of the "useful" current I_e to the current I_c, which represents an interference in analytical determinations. The rate of change in the polarisation potential V at low concentrations of the substance being studied can be decreased, in order to increase the ratio I_e/I_c, only to a certain limit. At low values of V, even without this, the small value of I_e decreases to such an extent that it becomes commensurate with background in the apparatus, and at high values of V the value of I_e is lost against a background which is many times greater than I_c. Thus decrease in the capacity current without change in I_e would mean an increase in the sensitivity of the method. For this reason, the developers of new apparatus have sought new methods of eliminating or decreasing the interference from I_c. For a long time, however, the solution to this problem in oscillopolarography was unsatisfactory. For example, in the slightly more sensitive electrochemical method of alternating-current polarography, the capacity current is eliminated by a variety of methods which make use of a special form of polarising voltage and special apparatus[3], whereas in oscillographic polarography, until recently the capacity current was eliminated only by linear compensation, which is insufficiently effective, however, since the capacity of the double layer shows a non-linear dependence on potential.

The earliest oscillographic polarographs had a comparatively low sensitivity, and the values of the parameters mentioned above were not achieved immediately. Comparatively recently, the difference method of oscillographic polarography has made possible the reliable determination of cadmium, lead, and zinc ions at concentrations down to 10^{-6} M, so that ordinary (not difference) oscillopolarography had an even lower sensitivity.

Subsequent work improved the electronic systems and the design of the individual blocks of oscillographic polarographs[16-18], and developed a circuit for the partial compensation of the capacity current[17]. One method for eliminating the capacity component and other interfering components of the current passing through the cell was the method of difference oscillographic polarography, developed by Pozdeev[19]. This makes it possible to increase both the sensitivity and resolving power of the analysis[5,15], since it gives a significant increase in the ratio I_e/I_c by presenting an oscillographic curve from simultaneous electrolysis of solutions in two identical cells. For example, this method can be used to eliminate the undesirable components of the current, associated with contamination of the electrolyte, the presence of large concentrations of other substances, and charging of the capacity of the double layer.

This method has been used to solve other problems[4], but it has several disadvantages. In addition to the fact that its use requires two cells, with a consequent increase in the complexity of the apparatus, the efficiency of this method of polarographic study is limited by the error in the subtracting assembly, and also by the difficulty of selecting two identical dropping mercury electrodes[9]. Thus the sensitivity of the difference method[14] achieved at present is 1.5×10^{-7} M, which is much greater than that of modern oscillographic polarographs operating with one cell (5×10^{-7} M) [20,21].

The theoretical and practical development of an oscillopolarographic method with a much lower level of capacity current than existing methods was achieved by Vyaselev[22]. The method was based on the principle of time selection, which makes it possible to separate the capacity and Faraday currents. In accordance with this principle, when a sudden change in potential is applied to a polarographic cell, the capacity current is damped more rapidly than the Faraday current. The current of the electrochemical reactions proportional to $t^{-1/2}$, whereas the capacity current is proportional to $e^{-t/RC}$, where R is the ohmic resistance of the cell and C the capacity of the double layer. Thus after a certain time interval from the moment when the sudden change in potential is applied, the current passing through the cell will be determined chiefly by the Faraday component. The idea of the possibility of using a step-like form of polarising voltage in oscillographic polarography was first put forward by Barker[23,24]. For a long time before Vyaselev's work[22], however, the idea was not realised, either theoretically or in practice. The theoretical study of the dependence of the diffusion current on the step-like polarising voltage showed that for step-like voltage, the measured values of the capacity current are in fact much smaller than those for a linear voltage[25,26]. This led to the development of an oscillopolarographic method in which the polarising voltage is applied in the form of sudden exponential increases[27]. Theoretical problems of oscillographic polarography with stepwise change in the polarising voltage were solved by

Vyaselev and Nigmatullin [25,26] and by Lingane and Christie [28,29]. The sensitivity of the method with step-like voltage (with respect to cadmium chloride solution) is 5×10^{-8} M, which is greater by an order of magnitude than that of the method using a linearly-changing voltage [26].

In addition to the difference method [19], differentiation of the oscillopolarographic curve [6,14,16,17] has been used to increase the resolving power. The analytical expression for the first derivative of the curve $I = f(E)$ was determined by Shekun [30], who showed by calculation that the height of the peak on the first-order differential oscillopolarogram $dI/dE = f(E)$ is a linear function of the concentration of depolariser; this makes it possible to use the relationship for quantitative analysis, as in classical polarography.

Unlike the first derivative of the classical integral polarogram, the oscillographic differential polarogram shows a negative peak as a consequence of a decrease in the current on the original curve, and the potential of its maximum does not coincide with $E_{1/2}$. This form of oscillopolarogram with negative peak makes the interpretation difficult, particularly in the study of multicomponent systems, and it is not convenient for analytical purposes.

Nigmatullin [31] was the first to show that for a reversible electrode reaction, the oscillopolarographic relationship $I = f(E)$ is a fractional derivative, of half-order, of the classical integral polarisation curve. On this basis, it was suggested that not ordinary differentiation, but half-order differentiation, that is so-called fractional differentiation, of the oscillographic curve be used to improve the resolving power of the method. The fractionally-differentiated oscillopolarogram obtained in this way corresponds in appearance to the first derivative of the classical integral polarogram, that is it does not have a negative peak and can be used for analytical purposes.

By combining the methods of difference oscillopolarography [19] and differentiation of the oscillopolarograms [6], Davis and Rooney [14] were able to obtain the second derivative of the oscillopolarogram, which gives good qualitative resolution with respect to potentials, but which is inconvenient for quantitative treatment.

Because of the mutual influence of different depolarisers, present simultaneously in the solution, on the shape of the peaks on the oscillopolarograms, quantitative calculations do not always have sufficient accuracy and reproducibility. To increase the accuracy of the measurement, Gokhshtein and Gokhshtein [32] proposed a method for extending the descending branch of the oscillopolarogram when the wave of another component was superimposed on it. The method gives satisfactory results if there is no appreciable capacity current; it can therefore be used successfully only at comparatively high concentrations of the substances being studied, when the capacity current is satisfactorily compensated by a linear method.

In oscillographic polarography with a polarising voltage of linear form, the relationships for the height and position of the peak on the oscillopolarogram are derived with the condition that the potential of the micro-electrode is a linear function of time [33,34]. As a consequence of the decrease in voltage across the ohmic resistances of the electrolytic cell and the elements of its circuit, however, this relationship is not observed for the change in potential under the conditions of the experiment. As a result, the oscillographic wave is extended, its height decreases, and the peak is displaced towards more negative potentials and becomes less sharp, so that the sensitivity of the measurements decreases. With very high ohmic resistances, the wave is completely "flattened", and the study becomes impossible. These phenomena have been observed experimentally, and in particular have been reproduced in an electric model [35-38] and have been the subject of discussion [39]. A special assembly has been designed [40] to compensate the cell resistance and obtain an oscillographic curve suitable for treatment, and also to increase the accuracy of the measurements. It successfully combines automatic compensation of the volume resistance with manual control, proposed by Valenta and Vogel [41]. The automatic compensation of the volume resistance is achieved by the oscillographic polarograph together with a three-electrode cell of special design. The method used for the controlled compensation of the volume resistance involves in practice a gradual increase in the feedback signal until the polarogram on the oscillograph screen corresponds to the theoretical. This form of compensation is less convenient, since in each specific case it requires the selection of the feedback signal in relation to the magnitude of the cell resistance. This method can be used, however, to estimate the magnitude of the compensated resistance.

Oscillographic polarography has recently become one of the highly sensitive methods which can be used for the analysis of traces of elements [42]. Despite the fact that data on the accuracy, sensitivity, and resolving power of this method have been published, it cannot be considered that these problems have been sufficiently fully studied from the methodological viewpoint.

It may be assumed that the dependence of the error in the measurement on the concentration of the substance being determined is of the form typical of micro-determinations [43], when the error increases close to the limit of the determination, since at this level of concentrations, the useful signal and the signal of the background (or blank experiment) are of comparable magnitude. The reliable measurement of signals at the level of the limit of the determination of substances and the "noise" of the oscillographic apparatus are metrological problems, and constitute one of the most important topics in measuring technology [44]. If the methods known as amalgam polarography with build-up (APB) [45] and film polarography are used, the sensitivity can be increased; these methods are examined in considerable detail in the literature.

Another method for increasing the sensitivity of polarographic determinations is based on the adsorption of the molecules of the depolariser on the electrode surface. Many reactions at an electrode take place with the participation of adsorbed species [46]. The concentration of these species at the electrode surface may be many times greater than their concentration in the volume of the solution. Thus when the polarographic voltage is applied to the cell, the reduction current in the first moments of time should be much greater than the value which might have been reached in the absence of adsorption; this makes it possible in principle to alter considerably the magnitude of the concentration minimum being determined.

The possibility of the practical realisation of this experiment was first demonstrated by Kalvoda and the present author [47,48] for the example of various organic substances (benzophenone, dibenzylmercury, etc.) sparingly soluble in aqueous alcohol, and thiosemicarbazones [49].

For the effective utilisation of the phenomenon of adsorption to increase sensitivity, the following conditions are obviously necessary [50]: 1) for significant "enrichment" of the electrode surface in adsorbed molecules, sufficient time is required for the establishment of adsorption equi-

librium at the micro-electrode in dilute solution; in some instances about 1 h has been necessary[46]; 2) since the quantity of adsorbed molecules at the surface of the micro-electrode is comparatively small, the oscillopolarogram must be recorded in a short time interval, that is it is necessary to select a suitable rate of polarisation; 3) the oscillopolarograms should be recorded with improved apparatus which makes it possible to eliminate the charging current of the double layer capacity, for example an oscillographic polarograph with step-like voltage[26,27,50].

The use of the phenomenon of adsorption to increase sensitivity opens up extensive possibilities in the analysis of organic substances by oscillographic polarography. Although the method of APB can be used successfully to determine traces of ions in solution, this is impossible for organic compounds, for reasons which are well understood. For some classes of organic compound containing groups which are active with respect to the electrode material, such as aldehydes, ketones, derivatives of urea and thiourea, thiosemicarbazones, organic compounds of sulphur, etc., which react with mercury at positive potentials[1] with the formation of the corresponding organomercury compounds or mercury sulphide[51,52], however, it is possible to use the principles of film polarography. This involves essentially preliminary electrolysis of the solution being studied at the potential of the initial level of recording of the $I = f(E)$ curve, as a result of which the compounds mentioned above are formed on the electrode surface in the form of a film; with cathodic polarisation of the electrode they are revealed as sharp peaks corresponding to the reduction of the corresponding substances, and this is used for analytical purposes. For thiourea, the minimal concentration which can be determined by this method is 10^{-7} M [52].

The sensitivity of the oscillopolarographic method can also be increased by making use of the formation of sparingly soluble substances, with low degrees of dissociation, in the solution[53-56]. Decrease in the activity of a substance leads to a decrease in the extent to which it is adsorbed on an electrode surface[53]. Since for sparingly soluble substances the activity is inversely proportional to the change in solubility, decrease in solubility will lead to an increase in the degree of covering of the electrode surface, that is adsorption.

The mechanism leading to the increase in the depth of the peaks under the influence of anions is still insufficiently clear. It is probable that in addition to a change in the Ψ'-potential in solutions containing anions which are readily adsorbed on the electrode, some contribution is made by adsorption-chemical interaction of the anions with the atoms of the reduced metal. From this it follows that when the sensitivity of an oscillographic polarograph is established with respect to a given substance (cadmium salts are usually employed for this purpose), it is necessary to indicate the composition of the background. An increase in sensitivity is facilitated by the formation not only of sparingly soluble substances, but also of complexes of the ions being determined with organic ligands, with a low degree of dissociation[13,57,58]. Thus cobalt is readily determined in plant materials, from the oscillopolarograms of its inner-complex compounds with dimethylglyoxime[58].

An example of a process similar to this mechanism of concentration is apparently provided by the extraction of various ions of uranium, zirconium, mercury, and the rare earth elements from aqueous solutions by organophosphorus compounds present in the adsorbed state on the surface of a stationary electrode[59]. In this instance it is assumed that coordinate bonds are formed between the metal and the organophosphorus compound in the surface layer[60], leading to the accumulation of the substance and hence to an increase in sensitivity. This method of increasing sensitivity has essentially not yet been used in oscillographic polarography.

Finally, mention must be made of another way of increasing the sensitivity of the oscillopolarographic analysis of organic substances—the use of the salting-out effect. In early work on oscillographic polarography, concentrated base electrolytes (1 M or more) were generally used to decrease the resistance in the polarographic cell. For a number of organic compounds, increase in the concentration of the background is not without an effect, since the organic compound is usually salted-out from solution. The salting-out of organic substances from concentrated solutions of electrolytes leads to an increase in their surface concentration[61]. Thus if the last effect is observed, the heights of the peaks or teeth on the oscillopolarograms will increase with increased concentration of the background electrolyte, and this leads to an increase in sensitivity. Thus Kalvoda[62] showed for derivatives of benzoic acid that with increase in the KF concentration to 10 M, the determination of these compounds becomes possible, whereas in a background of the usual neutral buffer, almost no capacity effects are observed on the oscillopolarograms of solutions of these derivatives.

2. Form of Oscillopolarographic Curves and the Mechanism of Electrode Reactions

A source of information on the nature of an electrode process and the composition of a solution being analysed is provided by the oscillographic curve, the form of which depends on a number of factors.

Firstly, the form of the curve, and in particular the position of the peak with change in V depends on the type of electrode process and its characteristic features[1]. In earlier work[51,52,63,64], conclusions regarding the nature of the electrode reaction were generally reached on the basis of the rate coefficient, or the so-called "Semerano criterion"[1,65]. Recently, various diagnostic criteria have been derived for the investigation of the nature of the various stages of an electrochemical process, associated with the transfer of electrons and involving conjugated chemical reactions. For this purpose, Nicholson and Shain[66] proposed the use of not only the form of the change in current at the peak I_p with change in V, but also the dependence of such parameters as the potential E_p, the half-peak potential $E_{p/2}$ (when the peak is "flattened" over several millivolts along the axis of potentials), the width of the oscillopolarogram (the extent of the curve along the axis of potentials between the abscissae E_p and $E_{p/2}$), the ratio of the heights of the anodic and cathodic peaks I_{pa}/I_{pk} with change in V, and also the dependence of the current function Ψ (the current function Ψ is defined by the expression $I_p/nFAC_0\sqrt{Da}$, where I_p is the current at the peak, A the area of the electrode, C_0 the volume concentration of the depolariser, a a kinetic parameter $a = nFV/RT$, and the other symbols have their usual significance) on V. These criteria were derived for the usual conditions of oscillographic polarography with an electrode, the surface of which does not change during the recording of the curve. It should, however, be noted that the form of the oscillopolarogram for a definite form of polarising voltage depends on the type of electrode

used[4,67,68], that is on whether the electrode is liquid or solid, spherical, flat, or film, etc., on the dimensions of the space next to the electrode[69], on the ohmic factors of the cell[39,70], which depend on the concentration of the background electrolyte, and apparently on the nature of the solvent[4]. If the oscillopolarograms are obtained as the plots of I against E at a mercury electrode with a very short dropping period of ~0.008 s, the form of the curves is identical to that of the usual classical curves[67]. If the surface of the mercury electrode changes during the recording of the oscillopolarograms, the most suitable criterion for the calculation of I_p for different V and arrests of the polarisation pulse is the moment when the curve reaches E_p [71]. In principle the method of oscillographic polarography makes it possible to determine a number of parameters characterising the electrode process, such as a, the transfer coefficient; D, the coefficient for the diffusion of the substance towards the electrode; n, the number of electrons taking part in the electrode reaction; k_s, the reaction rate constant; and ΔG, the standard free energy of activation of the discharge process. Moreover, it is possible to establish the nature of the separate electrochemical stages, complicated by chemical reactions, the reaction rate constants, and the orders of the reactions, and to detect the formation of intermediate species during electrolytic reduction or oxidation. Usually, the relationships for the calculation of the parameters have been derived without allowance for the adsorption of depolariser species on the electrode surface, as for example in Ref. 66, or with the assumption that the contribution of adsorption is slight. For organic compounds this is only a particular case. The use of oscillographic polarography to study adsorption phenomena will be examined below.

If an electrode process is controlled by the rate of diffusion and the electron transfer stage is reversible or almost reversible and is not complicated by chemical reactions, the corresponding oscillopolarograms have a sharp maximum. E_p in this instance is independent of the depolariser concentration. The value of I_p is determined by the familiar equations of Sevcik or Randles[33,34,72,73], is independent of the pressure on the dropping mercury[74], and is directly proportional to $V^{1/2}$. For reversible processes, the following relationships are applicable[66,75]:

$$E_{p/2} - E_p = \frac{0.057}{n}(1) \quad \text{and} \quad E_p = E_{1/2} - (1.109 \pm 0.002)\frac{RT}{nF} \qquad (2)$$

or for an indistinct peak $E_{p/2} = E_{1/2} + 1.09\,RT/nF$, where $E_{1/2}$ is the polarographic half-wave potential, and R, T, and F are familiar constants. From the descending branch of the oscillopolarograms at potentials 0.2 V more negative than E_p, it is possible to determine n from the equation

$$I_p/I = n^{1/2} \cdot \text{const} \qquad (3)$$

derived theoretically[76] and later found empirically[77], and also the diffusion coefficient of the depolariser D[76]:

$$I_{0.2} = 1.43 \cdot 10^5 \cdot n \cdot A \cdot C_0 \cdot V^{1/2} \cdot D^{1/2} \qquad (4)$$

where $I_{0.2}$ is the current for a potential of $(E_p + 0.2)$ V. For reversible processes with diffusion control, moreover, the quantity $\Delta E_{p/2}/\Delta \lg V$ is independent of V [66]. If the electrode is polarised by a triangular voltage pulse, for a reversible process, an anodic peak is observed in addition to a cathodic peak, the ratio I_{pa}/I_{pk} is equal to unity[66], and ΔE_{pak} is $0.057/n$ V[78]. Study of the dependence of ΔE_{pak} on V makes it possible to find comparatively simply the value of k_s—the heterogeneous rate constant for the electrode reaction[78]. The chief source of error in this determination is the non-compensated quantity IR, which depends on C_0, V, and the concentration of the background in the cell. With increase in I, the ohmic potential drop will be commensurate with ΔE_{pak} so that it is necessary to take precautions to eliminate it or to make allowance for this effect in the calculations.

For an irreversible electrode reaction with diffusion control, I_p is determined by Delahay's equation[79]:

$$I_p = 2.99 \cdot 10^{-5} \cdot n \cdot A(\alpha n_a)^{1/2} \cdot C_0 \cdot D^{1/2}V^{1/2} \qquad (5)$$

where n_a is the number of electrons taking part in the potential-determining stage ($0 < n_a < 1$). The form of the curve for an irreversible process depends on αn_a, whereas the heterogeneous rate constant k_s defines only the position of this curve on the axis of potentials, that is it depends on E_p. Since $\alpha < 1$, and $n_a < n$, it follows that I_p for an irreversible process is less than I_p for a reversible process. To determine n it is possible to use Eqns. (3) and (4), which are also applicable for an irreversible reaction with allowance for the coefficient α. The transfer coefficient is found from Matsuda's relationships[75]:

$$\alpha = \frac{0.048}{n(E_{p/2} - E_p)} \qquad (6)$$

Comparison of the experimentally observed value of I_p for an irreversible process with that calculated theoretically from Randles' equation[73] also makes it possible to estimate α from the equation[75]

$$\alpha = \left(0.9\,\frac{I_p^{\text{exptl}}}{I_p^{\text{theor}}}\right)^2 \qquad (7)$$

On going to irreversible processes, for example with increase in V [76], the sharp form of the maximum on the oscillopolarogram is smoothed out, and the curve extends further along the potential axis than that for a reversible reaction, and the slope of its central section is given by the expression[66]:

$$E_p - E_{p/2} = -1{,}857 \cdot \left(\frac{RT}{\alpha n_a F}\right). \qquad (8)$$

The anodic peak for irreversible processes is absent, or else its potential is much greater than the theoretically permissible difference ΔE_{pak}. It has been shown that for an irreversible reaction the current passing in the initial section of the oscillopolarogram is independent of V [66,80]. E_p and $E_{p/2}$, however, are functions of V [66]:

$$(E_{p/2})'' - (E_{p/2})' = (E_p)'' - (E_p)' = \frac{RT}{\alpha n_a F} \ln \sqrt{\frac{V'}{V''}} \qquad (9)$$

that is with an irreversible process a cathodic shift of the peak or half-peak potentials by about $0.03/\alpha n_a$ is observed for each tenfold increase in the rate of polarisation. From the relationship for the current and potential of the electrode for irreversible reduction[66], as for Gokhshtein's equation[76], it follows that the plots of $\lg I_p$ against $(E_p - E_0)$, where E_0 is the formal electrode potential, for different V are given by straight lines with slope equal to αn_a, and with distance between them proportional to k_e°—the rate constant for direct electron transfer. This relationship is convenient for finding the kinetic parameters of an electrode reaction, although this requires

a change in V by several orders of magnitude. The value of k'_e can also be found from Matsuda's equation[75]:

$$\lg k'_e = 1.1339 - \lg f/\sqrt{D} + {}^1/_2 \lg(\alpha n_a) V + \frac{\alpha n_a E_p}{0.0591} \qquad (10)$$

where E_p is given relative to the potential of the hydrogen electrode, and f is the activity coefficient. This equation also shows that k'_e depends on E_p and V. The standard free energy of activation ΔG is given by the equation derived[81] from the equation of Delahay[79] and the Gokhshteins[32]:

$$\Delta G = F[\alpha n_a(E_a - E_p) - 0.0591 \lg I_p/nAC_0 + 0.54 + 0.0591 \lg 10^8 \cdot \rho] \qquad (11)$$

where E_a is the potential of the reference electrode, and ρ the distance to which the depolariser species approaches the electrode. Fig. 1 gives some of the graphs which

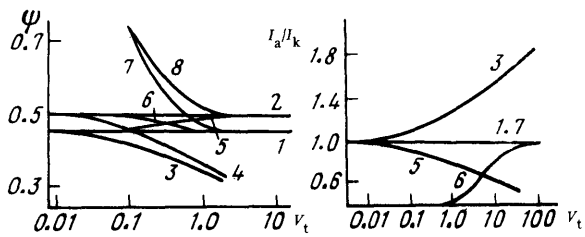


Figure 1. Dependence of the current function Ψ and the ratio I_a/I_k on the rate of polarisation[66]: *1*) reversible and *2*) irreversible charge transfer; *3*) reversible and *4*) irreversible charge transfer preceded by chemical reaction; *5*) reversible electron transfer, followed by a reversible chemical reaction; *6*) reversible charge transfer, followed by irreversible chemical reaction; *7*) catalytic reaction with reversible and *8*) irreversible electron transfer.

serve as diagnostic criteria for the main types of reaction mechanism[66]. It should be noted that Eqns. (5)–(11) are applicable with the condition that αn_a is independent of potential. Methods for finding the rate constants of the chemical reactions preceding, taking place in parallel with, or following the transfer of electrons have been examined by a number of authors[66,82-95]. Compared with classical polarography, oscillographic polarography makes it possible to extend the range for the determination of these quantities by four orders of magnitude. From the theory of kinetic currents in polarography it follows that for an electrode process taking place according to the scheme $L \underset{k_B}{\overset{k_f}{\rightleftharpoons}} O \overset{n_e}{\rightleftharpoons} B$, the upper limit is given by the expression $k_B = 200\ \tau^{-1}K^{-2}$ [46,82], where τ is the duration of electrolysis or the dropping period of the electrode, and $K = k_f/k_B$ the equilibrium constant for the chemical reaction. It follows from the last expression that in order to find the constants for very fast chemical reactions it is necessary to decrease the duration of electrolysis. In oscillopolarography, τ depends on the rate of polarisation. If it is assumed that $V = 500$ V s^{-1}, and that the polarisation pulse varies in the region of 1 V, then the duration of electrolysis is less than 2×10^{-3} s, and this makes it possible to study extremely fast chemical reactions taking place at the electrode. The practical restrictions here are that at such high values of V, there is a marked increase in I_C, as mentioned above. If the methods of difference oscillopolarography[19] or a stepped polarising voltage[26-28] are used, however, this restriction can be eliminated to a considerable extent. Essentially, for each chemical reaction preceding electron transfer, it is possible to find a range of V for which the $I = f(E)$ curves become independent of the rate of the chemical reaction. In this case the current recorded will be controlled by the diffusion of the substance O to the electrode and will correspond to a state of equilibrium between L and O. The value of K in this case is determined independently of the values for the rate constants of the chemical reaction. This method was used to determine the equilibrium constant for the hydration of formaldehyde[85] and the isomeric pyridine aldehydes[86].

The case where the reversible transfer of electrons is preceded by a chemical reaction of first order was examined by Saveant and Vianello[82]. Using the method of dimensionless parameters, they derived relationships characterising the dependence of the current function on the electrode potential for different values of K and k ($k = k_f + k_B$). The change in the parameter $\lambda = \frac{RT}{nF}\frac{k_f + k_B}{V} = \frac{kTk}{nFV}$ within certain limits makes it possible to change from pure diffusion current to currents controlled by a preceding chemical reaction. For $K > 20$ the current–potential curves have the usual form characteristic of diffusion-controlled processes. At smaller values of K the curves show kinetic limitation. For $K < 0.5$ the range of existence of kinetic currents is determined by the value of λ in the range

$$0.025 < \lambda < \frac{100}{K^2} \qquad (12)$$

For $\lambda < 0.025$ the rate of the chemical reaction is so low compared with V that during the polarisation pulse, significant formation of the substance O from L does not take place, and the current is controlled by the diffusion of O, the concentration of which is determined by the equilibrium $L \rightleftharpoons O$. For very low values of K the diffusion currents are very low and difficult to measure. However, since I_p is proportional to $V^{1/2}$, the measurement can be made at suitable values of V. For $\lambda > 100/K^2$ the rate of the chemical reaction is so great compared with V that the equilibrium at the electrode is established almost instantaneously, so that I_p is determined by the volume concentration of the depolariser. The $I = f(E)$ curves then show a cathodic displacement by an amount $\frac{RT}{nF}\ln\frac{K}{1+K}$ with increase in V by one order of magnitude. For intermediate values of λ, given by Eqn. (12), the currents are limited by the kinetics of the chemical reaction. If V changes in the range 0.1–500 V s^{-1}, the measured kinetic currents are determined by the range $0.1\ s^{-1} < k < 2 \times 10^6/K^2\ s^{-1}$ (for 25°). The form of the anodic peak on the oscillopolarograms obtained with a triangular voltage pulse is influenced by a preceding chemical reaction to a much smaller extent than the form of the cathodic peak[66]. In the work cited[66], a change in the quantities I_a/I_k, $\Delta E_{p/2}/\Delta \lg V$ and I_k with change in V was also detected, and it was recommended that these be used as diagnostic criteria. A particular case of reversible electron transfer with a preceding chemical reaction,

considered above, is a process of the type $L \underset{k_B}{\overset{k_f}{\rightleftharpoons}} 2\,O$; $O \overset{ne}{\rightleftharpoons} B$ [83]. For this the form of the oscillopolarogram depends on the value of a certain dimensionless parameter θ, proportional to the product $\frac{(k_B)^{1/2}}{V^{1/2}} \cdot K^{3/4} \cdot C_0^{-1/4}$ [83]. For very small values of θ the $I = f(E)$ curves have the form of integral polarograms, for which $E_{1/2}$ is given by the equation (for 25°):

$$E_{p/2} = E_{1/2} + \frac{0.041}{n} + \frac{0.03}{n}\lg n - \frac{0.03}{n}\lg k_B - \frac{0.015}{n}\lg K + \frac{0.03}{n}\lg V + \frac{0.015}{n}\lg C_0 \qquad (13)$$

For high values of θ the reduction current is diffusion controlled, and $E_{p/2}$ is not now dependent on V

$$E_{p/2} = E_0 + 0.01 + \frac{0.03}{n}\lg K - \frac{0.03}{n}\lg C_0 \qquad (14)$$

(with the condition that the diffusion coefficients of O and B have similar values) where E_0 is the normal redox potential of the O/B complex.

Irreversible transfer of an electron with a *preceding* chemical reaction of first order was examined in detail by Nicholson and Shain[66], who give the dependence of the calculated values of the current function on the parameters of the chemical reaction (K, $k_f + k_B$) for which equilibrium is established slowly, compared with discharge. Voloshin[84] used these calculations in a study of electrochemical processes with a preceding reversible chemical reaction of higher order $L + mz \rightleftharpoons B$ and found that a change in the concentration of z displaces the potential of the peak in the same way as $E_{1/2}$ changes with the pH of the solution for processes preceded by protonisation[46]. For this type of electrode reaction it is useful to study the dependence of I_p and $\Delta E_{p/2}/\Delta \lg V$ on V.

A paper already cited[66] discussed for the first time the case where the *rapid transfer* of electrons according to a reaction $L + ne \rightleftharpoons O$ is followed by a *reversible chemical* reaction $O \underset{k_B}{\overset{k_f}{\rightleftharpoons}} B$ (if the electron-transfer stage is retarded, the subsequent chemical reaction does not influence the form of the oscillopolarogram). A change in the value of the parameter $\xi = K\sqrt{\frac{nFV}{RT(k_f + k_B)}}$ by almost three orders of magnitude has little influence on the magnitude of the current function, so that to study the subsequent chemical reactions it is convenient to use the displacement of E_p with V. With change in the parameter ξ by one order of magnitude, E_p undergoes a cathodic displacement of almost $60/n$ mV, and tabulated data[66] can be used to estimate the parameters of the chemical reaction. The subsequent reversible chemical reaction has a marked influence on the anodic peak. It should, however, be noted that in this instance the depth of the anodic peak depends on the amplitude of the polarisation. Thus the dependence of the ratio I_a/I_k on ξ for the electrode reaction being considered must be obtained for some selected amplitude of polarisation.

If the *reversible transfer* of electrons is followed by an irreversible chemical reaction, taking place at a low rate, it has almost no influence on the form of the oscillopolarogram. For high values of the parameter RTk/nFV, however, the displacement of the potential of the cathodic peak with V can be used for a kinetic analysis[66]:

$$E_p = E_{1/2} - \frac{RT}{nF}\left(0.78 - \ln\sqrt{\frac{RTk_f}{nFV}}\right) \qquad (15)$$

It follows from Eqn. (15) that increase in the expression under the square root sign leads to an anodic displacement of E_p, whereas for the previous example a displacement of E_p towards cathodic potentials was noted. When the electrode is polarised by a triangular voltage pulse, useful information on the chemical reaction is obtained from the dependence of the quantity I_a/I_k on V, if allowance is made for the amplitude of the polarisation (or the time taken for E for the electrode to change from $E_{1/2}$ to the final polarisation potential)[66]. Saveant and Vianello[87] derived an expression for the dependence of E_p on C_0 for the depolariser and V for the case where the deactivation of the electrode products takes place as a result of their bimolecular interaction. From these equations it follows that the value of E_p should be displaced with increase in V, and $\frac{\Delta E_p}{\Delta \lg V} = \frac{RT}{nF}\left(\frac{1}{m+1}\right)$; with increase in C_0 the quantity E_p becomes more positive and $\frac{\Delta E_p}{\Delta \lg C_0} = \frac{m-1}{m+1}\cdot\frac{RT}{nF}$, where m is the order of the reaction with respect to the electrode products (for dimerisation, $m = 2$). The authors cited[87] point out that from the nature of the dependence of E_p on $\lg C_0$ it is possible to distinguish a process with retarded electron transfer from a process in which reversible electron transfer is followed by rapid dimerisation of the electrode products.

Electrode reactions with order greater than unity have been studied[88]. The $I = f(E)$ curves for polarisation of the electrode by triangular pulses were calculated by the published method[66] for processes $mO + ne \rightleftharpoons qL$ ($m > 1$), controlled by diffusion. It was found that for $m = 2$ and 3, the peaks are lower and broader than the peaks corresponding to a first-order reaction, examined above[66]. The theoretical calculations were verified experimentally for the example of the dissolution of mercury in potassium cyanide solutions ($m = 2$ or 3, depending on the cyanide concentration).

The catalytic reaction, in which the reversible transfer of electrons to the molecule of the depolariser O is accompanied by its parallel regeneration under the influence of the catalyst Z,

$$O + ne \rightleftarrows B, \quad B + Z \xrightarrow{k_f'} O$$

was discussed in detail by Saveant and Vianello[89], and later by Nicholson and Shain[66]. For a given value of k_f' and concentration of the catalyst, change in V gives a family of curves with a common asymptote, the ordinate of which is independent of V and is determined by the expression

$$I_{lim} = nFA\sqrt{C_Z D k_f'} \qquad (16)$$

Eqn. (16) can be used to find k_f'. The parameters of the catalytic reaction can be studied by means of triangular voltage pulses, for which the form of the oscillopolarograms depends on the magnitude of RTk_f'/nFV [66],

and also from the dependence of $\Delta E_p/\Delta \lg V$ on V. For a catalytic system of this type the ratio I_a/I_k is equal to unity and is independent of V, as in the case of reversible transfer of electrons, not complicated by chemical reactions[66].

For a system in which *the electrochemical and chemical stage* of catalysis are *irreversible*, the results obtained are analogous to the previous example, but the peaks in this instance will have a smaller height and will be slightly more extended along the axis of potentials. The form of the wave depends on the parameter $\frac{RTk'_f}{\alpha n_a FV}$. Saveant and Vianello[90] recommend for the determination of k'_f the measurement of the dependence of the ratio of the limiting catalytic current to the current for a given rate of polarisation on V.

An interesting type of electrode reaction is that corresponding to processes which take place by the so-called ECE mechanism, that is when there is a chemical reaction $L \overset{n_1 e}{\rightleftharpoons} O \overset{k_f}{\rightarrow} B \overset{n_2 e}{\rightleftharpoons} Z$ between the electrochemical stages. The oscillopolarograms may have different forms, depending on the relative ease of reduction of the depolariser species L and B, and also on the extent to which the chemical reaction and the electron transfer stage are reversible. In general, the study of its dependence on the parameters of the electrode reaction is very complex. Examples where the chemical stage is irreversible[92-94], and the transfer of electrons takes place rapidly[92-94] or is retarded[92], have been examined. If both transfers of n_1 and n_2 electrons are reversible, and the difference in the ease of reduction of the species L and B (that is their $\Delta E_{1/2}$ values), is sufficiently large and it is more difficult to reduce B than L, then the curves contain two peaks, the form of which is determined by the parameter RTk_f/nFV and the ratio n_2/n_1. At low values of this parameter the second peak is not observed, and with increase in the parameter the peak height increases. The form of the anodic peaks depends to a considerable extent on k_f and the extent of polarisation of the electrode, so that it is difficult to obtain information on the process from it. The calculated values of the current function for the reversible and irreversible transfer of electrons for different values of the kinetic parameter n_2/n_1 and $E_{1/2}$ [92] make it possible to determine k_f for the chemical reaction included. For example, a detailed study was made of the reduction of *p*-nitrosophenol, which takes place by an ECE mechanism[93]. The values obtained for k_f show good agreement with results obtained by other electrochemical methods. For cases analogous to *p*-nitrosophenol (for $n_1 = n_2$), it is convenient to determine k_f by means of the equation

$$I_k/I_d = \frac{0.4 + \frac{RTk_f}{nFV}}{0.396 + \frac{RTk_f}{nFV} \cdot 0.469} \qquad (17)$$

where I_k is the height of the kinetic peak, measured at a certain value of V, and I_d is the magnitude of the current, calculated with the assumption that there is no chemical reaction, or measured at high values of V.

Despite the extensive possibilities provided by oscillographic polarography for the study of the mechanism of electrode reactions, the number of papers in which the theory of the method has actually been used for this purpose is small. Thus the value of k_s for the reduction of the cadmium ion in 1 M KCl has been determined[78], and values of α, n, k_s, D, and the free energy of activation for reduction at a dropping mercury electrode (d.m.e.) have been found for the ions of europium[96], indium and antimony[97], and silver in alkali metal nitrate solutions[98], and of silver, cadmium, lead, copper, and indium in a eutectic mixture of sodium and potassium nitrates at 245° at a platinum electrode. In the last work cited, it was established in which of the systems the reduction product is oxidised to the oxide by nitrate, or the metal forms an alloy with the electrode material. The reversible discharge of a substance with constant activity, accompanied by irreversible combination of the reaction product at the electrode has been studied in detail for the example of the anodic dissolution of mercury in sodium sulphide solutions[100].

Study of the mechanism of the reduction of sulphur dioxide in acid media at a mercury electrode showed that under these conditions, hydrogen sulphide and elementary sulphur may be formed[101].

The method of oscillopolarography with triangular scanning of the voltage has been used to study the stability and ligand exchange of mixed porphyrin complexes of Fe^{III} with cyanide and pyridine in solution at a platinum electrode[102] and ligand exchange in the product of the reduction of Fe^{III} acetylacetonate in acetonitrile[103], and to study the kinetics of an electrode process involving ionic complexes of zinc with hydroxide ions and ammonia at a stationary mercury film electrode[104]. The method was used to study the kinetic parameters and the nature of the reduction of the nitriles of acrylic, vinylacrylic, and cinnamic acids[105] at a mercury electrode, Cupferron at a carbon paste electrode[106] and a d.m.e. [107] in aqueous alcohol, diphenylpicrylhydrazyl in tetrahydrofuran at a platinum electrode[108], and isomeric cyanopyridines[109]. Study of the dependence of E_p for the peak on V and C_0 for the tropylium cation showed that in its one-electron reduction at a d.m.e., dimerisation of the radicals takes place[110]. In the reduction of benzanthrone in acidic aqueous alcoholic solutions, however, in addition to the peak corresponding to the transfer of one electron with subsequent dimerisation of the product, at high rates of polarisation a second peak produced by further reduction of the radical is detected[111]. From the nature of the I_p and V relationships observed in a study of the catalytic currents of cystine, cysteine, and albumin in the presence of cobalt ions, it was found that the magnitude of the catalytic effect is determined not only by the rate of the catalytic reaction but also by the rate of decomposition of the active complex[112].

It was noted above that the ohmic potential drop in the cell distorts the shape of the oscillopolarograms, that is it influences I_p, E_p, and their dependence on V, so that the determination of the kinetic parameters of the electrode reaction from these curves is impossible. Moreover, the non-compensated capacity current makes it impossible to use experimentally the high rates of change of potential which are often necessary for kinetic measurements. This is the reason for the comparatively small extent to which oscillopolarography is used in the study of the mechanism of electrode processes. A considerable restriction in the use of Eqns. (1)–(17) is caused by the phenomenon of adsorbability (particularly of organic depolarisers), which was not taken into account in the theoretical derivation of Eqns. (1)–(17). Oscillographic polarography can be used, however, to make a special study of the adsorption of organic compounds on

an electrode surface[1,113] and in some instances to estimate the contribution which it makes to an electrochemical process.

For substances which are not depolarisers, the method is based on the study of the change in I_C when these substances are added to the polarographic solution at different values of V. The principles of the method have been discussed[1,113]. Delahay believes[114] that the method gives erroneous results if allowance is not made, where necessary, for the fact that the adsorption is controlled by diffusion. Moreover, the method is restricted to the range of comparatively concentrated solutions of background electrolyte (greater than 0.1 M), since it does not allow for the resistance of the solution in the cell. The analytical application of this method is well known[1]. In addition to the quantitative determination of adsorbed substances from appropriate calibration curves, which generally have the form of the Langmuir isotherm, the method makes it possible to reach conclusions regarding the nature of the surface-active substances and some of their properties. The adsorption peaks with the form of a sharp maximum are characterised by a ratio $\lg I_p/\lg V$ equal to 1 (the so-called "Semerano coefficient"[65]). The situation is more complicated when the substance exhibiting surface activity is a depolariser. In this instance oscillographic polarography makes it possible to determine the adsorbed quantity of reacting substance by integration of the oscillopolarogram[115]. The integration is carried out in different ranges of potential, and for each range of integration, graphs are constructed giving the dependence of Q the quantity of electricity passed on $V^{-1/2}$. For reversible processes with only one electrochemical stage and with depolariser supplied by diffusion, this dependence is given by a straight line passing through the origin of coordinates. If reduction of the adsorbed depolariser takes place at the electrode, the straight line obtained by plotting Q against $V^{-1/2}$ has an intercept on the ordinate axis (that is as $V \to \infty$) corresponding to the quantity of electricity Q consumes in the reduction of the depolariser on the electrode surface. This method of extrapolating the values of Q to $V \to \infty$ is based on the fact that for volt-ampere oscillopolarograms of reversible processes, the current at each point of the curve is proportional to $V^{1/2}$. Comparatively recently, it was shown[116] that for irreversible processes, the area of the initial sections under the current–potential curves is independent of V (since in these regions I is determined by the rate of the actual irreversible electrochemical reaction), so that in these instances the observed dependence of Q on V is more complex, and this makes the correct extrapolation to $V \to \infty$ difficult. This method was used to study the reversible reduction of adsorbed chloranilic acid[117]. One can agree with the view[118] that this method has no advantage over the charging-curves method. To achieve the accuracy given by the recording of the charging curves, volt-ampere polarography makes more rigorous demands on the apparatus and the conduct of the experiment than the charging-curves method.

The theoretical influence of various factors on the form of the oscillopolarograms for processes involving an adsorbed depolariser has been studied by a number of workers.

When depolariser species are adsorbed, the potential–current curves after the maximum show a current drop which is much sharper than that for diffusion-limited processes, and the transfer coefficient, according to Semerano[65], is greater than 0.5. In actual fact, for diffusion limitation the current decreases comparatively slowly with time, as the diffusion layer becomes broader, in proportion to $t^{-1/2}$. On reduction of a substance in the adsorbed state, however, higher values of the currents are observed at the peak, and this is followed by a sharp decrease in the current as a result of the exhaustion of the adsorbed depolariser to a level corresponding to its rate of supply by diffusion from the depth of the solution.

Wopschall and Shain[119,120] recently studied the form of the volt-ampere curves for the reversible reduction of a depolariser with strong and weak adsorption of the depolariser on the electrode surface in accordance with Henry's or Langmuir's relationships. The curves obtained with a linearly-polarising voltage of triangular form were studied. The theoretical curves for the system without complication by adsorption are compared with those with adsorption of the depolariser or the product of its reduction in Fig. 2. Weak adsorption of the depolariser leads to a slight increase in the height of the cathodic peak relative to the system without complication, and to a smaller increase in I_a on the anodic branch of the curve.

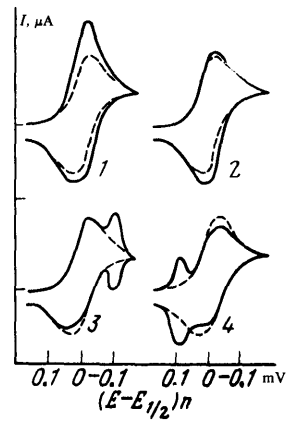


Figure 2. Theoretical forms of the oscillopolarograms for reversible electron transfer, complicated by adsorption[119]: *1*) weak adsorption of depolariser; *2*) weak adsorption of reduction product; *3*) strong adsorption of depolariser; and *4*) strong adsorption of its reduction product. The broken lines correspond to the systems not complicated by adsorption.

It is suggested that the dependence of the currents I_k and I_a on V and C_0 be used as diagnostic criteria. For high values of V the quantity of substance diffusing is small compared with the quantity of adsorbed substance reacting on the electrode surface, and for high values of V the opposite applies. Thus with increase in V the current increases relative to the value characteristic of the diffusion process for a given V. Fig. 3 gives a graph showing the dependence of the ratio of the current function Ψ (with adsorption of the depolariser) to the value 0.446 (for the process with complication by adsorption) on V. Change in the rate of polarisation also influences the magnitude of the reversible anodic peak, although its increase relative to the peak without complication by adsorption is slightly smaller than that for the cathodic peak (because of partial diffusion of the reduction product into the depth of the solution during the scanning of the polarisation pulse).

Increase in V, however, leads to a decrease in this loss of substance from the electrode surface, and the current also increases more rapidly relative to the process not complicated by adsorption. The graph giving the dependence of the ratio I_a/I_k on V has the form shown in Fig. 4, from which it can be seen that at low values of V the fraction of the current depending on adsorption becomes insignificant, and the ratio $I_a/I_k = 1$, as for the simple process. The observation that adsorption has a smaller influence on the form of the curves and the height of the peak at low values of V is a general feature of oscillopolarography, so that to decrease the effect of adsorption it is necessary to use low values of V. For weak adsorption, the fraction of the current corresponding to the adsorbed depolariser decreases with increase in C_0, and at high values of C_0 the current function Ψ takes values which are the same as those for the process without the adsorption of depolariser: this is illustrated in Fig. 5. To observe these effects, however, it is necessary to change C_0 by three orders of magnitude, and this is not always possible.

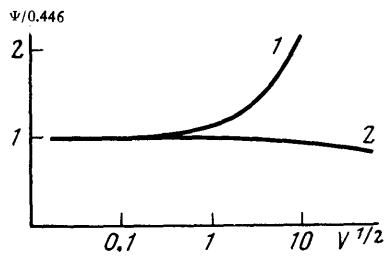


Figure 3. Dependence of the function $\Psi/0.446$ for the cathodic peak on V for weak adsorption of depolariser (*1*) and its reduction product (*2*) [119].

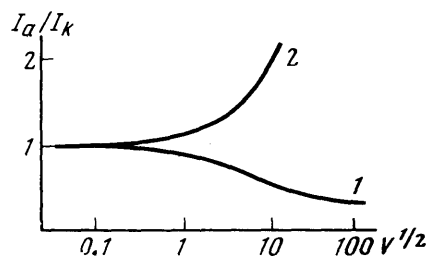


Figure 4. Dependence of the ratio I_a/I_k on V for weak adsorption of depolariser (*1*) and the product of its electrode reaction (*2*); duration of polarisation pulse after the half-wave potential $180/n$ mV [119].

An increase in the height of the anodic peak for an adsorbed reduction product relative to the peak in the absence of adsorption is usually observed when the product of the electrode reaction has been unable to diffuse into the volume of the solution during the scanning of the polarisation pulse. If the rate of polarisation is low, part of the substance is lost from the electrode surface during the passage of the pulse between the cathodic peak and the start of the anodic process, and this influences the depth of the anodic peak. This time depends on the amplitude of the pulse, so that the magnitude of the latter must be taken into account in measurements of this kind. For weak adsorption of a reducing agent, according to Wopschall and Shain[119], the cathodic peak, is only slightly displaced towards more positive potentials with increase in V, whereas the depth of the anodic peak increases appreciably and the ratio I_a/I_k also increases (see Fig. 4).

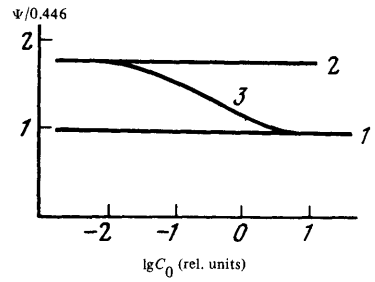


Figure 5. Dependence of the cathodic function $\Psi/0.446$ on C_0 for a system not complicated by adsorption (*1*) and for adsorption of the depolariser according to Henry's law (*2*) and Langmuir's law (*3*) [119].

At the same time, Wopschall and Shain[119] examined the case of *strong adsorption* of the depolariser or the product of its reversible electrode reaction, obeying the Langmuir isotherm.

If the product of the electrolytic reduction is strongly adsorbed on the electrode surface, the oscillopolarograms show two peaks. The first peak is an adsorption peak (its current is I_{ads}), and the second is associated with the supply of depolariser species to the electrode by diffusion (I_d) (see Fig. 2). The difference in the potentials of these peaks ΔE depends on C_0 and to some extent on V, but is determined chiefly by the nature of the adsorbed species. For low values of C_0, the ratio I_{ads}/I_d is less than 1, and the adsorption parameters are found from the half-width of the adsorption peak, ΔE for the peaks, and the dependence of I_{ads}/I_d on V and C_0. For high values of V, the preliminary adsorption peak may have diffusion character, and the diffusion peak, that is I_d, may be absent. A more detailed treatment of this example of adsorption can be found in the original paper[119].

Independently, Laviron[121] examined the influence of the adsorption of depolariser on the form of the oscillopolarograms for the reversible transfer of electrons for the example of the reduction of Methylene Blue. For $C_0 < C_{max}$, where C_{max} is the depolariser concentration at which saturation of the electrode surface takes place and the current at the peak is no longer dependent on the concentration, I_p is given by the expression

$$I_p = 6.96 \cdot 10^5 \cdot A \cdot n^2 \cdot V \cdot C_0 D^{1/2} \cdot t_1^{1/2} \qquad (18)$$

where t_1 is the time, given by the arrest before the polarisation pulse and the duration of its scanning before the peak. For $C_0 > C_{max}$, that is when the current at the

peak corresponds to the limit of the Langmuir isotherm, the value of I_p is given by the equation

$$I_p = 9.4 \cdot 10^5 \cdot A \cdot n^2 \cdot V \cdot \Gamma_{max} \quad (19)$$

where Γ_{max} is the quantity of substance adsorbed on the electrode surface. Laviron's equations, derived theoretically[121], make it possible in a number of instances to calculate the adsorption characteristics from the magnitude of the currents at the oscillographic peak.

A theoretical and experimental study of the influence of adsorption on the form of the curves for compounds undergoing irreversible reduction was made for the example of 1,2-dipyridylethylene[122]. Laviron based this study on the same premises and the assumptions[121] that the adsorption equilibrium at the electrode is displaced towards the adsorbed form of the depolariser, that is that the rate of adsorption is high and is not limited by the rate of formation of the film (at all concentrations). In this instance the current at the peak is given by the expression

$$I_p = 1.38 \cdot 10^6 \cdot n(\alpha n_a) \cdot A \cdot \Gamma_{(t_1)} V \quad (20)$$

where $\Gamma_{(t_1)}$ is the quantity of substance adsorbed in time t_1 (see above). The potential at the peak is displaced by an amount $0.059/\alpha n_a$ (at 25°) with change in V by one order of magnitude. Laviron's relationships[122] can be used to determine various parameters of the electrochemical reaction from the form of the peak.

It has been found for *m*-substituted nitrobenzenes that the current at the peak and the rate coefficient for the nitro-group depends on the nature of the substituent in the nitrobenzene molecule[64]: the higher the observed peak, the sharper the decrease in the current after the maximum (sometimes as far as the background current) and the greater the Semerano coefficient. The wave for the nitro-group appears on the curves in a range of potentials extremely favourable for adsorption. The changes in I_p, the form of the curves, and $\lg I_p/\lg V$ take place in parallel with the change in the depression of the differential capacity of the electrode in the presence of various nitro-compounds. The difference in the adsorbability of *m*-substituted nitrobenzenes is attributed to structural factors, and also to differences in the solubilities of the substances. The series studied show a tendency for I_p and $\lg I_p/\lg V$ to increase with decrease in the solubility. Analogous relationships were observed for various hydrazones[64], for which the irreversible four-electron wave appears on the curves in a wide range of potentials from −0.4 V to −1.4 V, depending on the nature of the substituent. As the reduction potential approached the point of maximal adsorption with the introduction of substituents facilitating discharge at the electrode, the peak mm on the oscillopolarogram became sharper, and the current at the peak increased, but $\lg I_p/\lg V$ exceeded 0.5, and this took place in parallel with the increase in the depression of the differential capacity. The form of the peak and the rate coefficient are also influenced by the concentration of depolariser[64,117]. In some instances the curves for a given depolariser may show two reduction current components: a surface component—a sharp peak, and a volume component—with a diffusion drop. Each of these components of the current has its own characteristic Semerano coefficient[64,117]. These phenomena on the oscillopolarograms agree with the theoretical ideas of Wopschall and Shain[119].

The adsorbability of substances on the electrode surface also explains the slight increase in the current at the peak with increased duration of the arrest before the application of the polarisation pulse, and the displacement of the initial level of recording of the curve away from the peak; this is particularly noticeable at low values of C_0. It should be noted that volt-ampere oscillopolarograms are generally recorded under conditions in which adsorption equilibrium at the electrode is not established. Adsorption with control by diffusion is retarded for strongly adsorbed substances at low volume concentrations. Convection, that is mixing of the solution, increases the rate of this process. A considerable time is sometimes necessary for equilibrium to be established (up to tens of minutes, for example in Ref. 50). Slow attainment of equilibrium at the electrode is apparently the reason for the production of hysteresis loops on current–potential curves[64]. Recently, Kalvoda[123] also emphasised that is it necessary, in the analysis of solutions with low concentrations of substances, to take account of the possibility that the establishment of adsorption equilibrium at the electrode is slow. Adsorption phenomena have also been discussed by Hale and Greef[124].

III. ANALYTICAL APPLICATIONS OF OSCILLOGRAPHIC POLAROGRAPHY

Modern forms of oscillographic polarography have developed towards an increase in sensitivity and resolving power in the study of chiefly inorganic materials. In the practical application of oscillopolarography in the last twenty years the greatest emphasis has been on the study of various ions in solution. As a result of the development of APB, oscillographic polarography has had to give some ground in inorganic analysis, since the APB method is more sensitive, and the apparatus is simpler. As already noted, however, the APB method has only a limited range of practical applications in the analysis of organic compounds, and in this field, among various electrochemical methods for the determination of small concentrations of organic substances, oscillographic polarography has recently found some applications.

1. Inorganic Analysis

The largest number of papers deal with the study of oscillopolarographic behaviour and the development of methods of determination in solution for ions undergoing reversible reduction at a d.m.e. Thus the influence of various factors on the nature of the electrochemical reduction of cadmium ions has been studied. The influence of the nature of the background electrolyte on the height of the peak for cadmium[125,126] in neutral solutions has been established. In the presence of halide anions and a trace of oxygen, the $I = f(E)$ oscillopolarogram in the potential region for the reduction of Cd^{2+} contains two peaks instead of one[125]. The explanation for the production of the peak at more negative potentials is that some of the Cd^{2+} ions at the electrode combine with OH^- ions (formed by the reduction of O_2) to form the sparingly soluble hydroxide, which is adsorbed by the electrode and subsequently reduced. The addition of gelatin or methylcellulose leads to a decrease in the height of this peak, until it disappears completely. The peak is also eliminated by acidification of the solution. This peak has been described as an oxygen peak[126], and it was later shown that its production requires a reaction taking place in parallel with the discharge of cadmium ions and bringing

about the electrochemical generation of OH^- ions. Study of the simultaneous reduction of cadmium ions and bromate anions at a d.m.e. by means of multi-cycle oscillographic polarography with a linearly changing potential[126] showed that the discharge of bromate ions can provide a source of hydroxide ions. Subsequently, a direct proportionality was established[127] between the height of the cadmium peak and the pH of the solution in the pH range 4–6.4. Thus in the presence of O_2 the sensitivity of the determination of Cd^{2+} depends on pH. Cadmium, lead, and thallium, which react reversibly at the electrode, have been the objects of a large number of studies by volt-ampere oscillopolarography. The chief results are summarised in the Table.

Oscillopolarographic study of inorganic ions at a mercury electrode.

Ion	Materials studied and conditions of polarography study	Results obtained	Refs.
1	2	3	4
Cadmium	Ammonia–ammonium salt buffer	Influence of V on reduction	128
	Halide solution	Influence of the nature of the background ion on the rate coefficient, the role of adsorption, and the mechanism of reduction	63
Cadmium and zinc	1 M NH_4Cl, 4 M NH_4OH in the presence of atmospheric oxygen	Selection of optimal conditions for analysis	129
Cadmium, thallium, and zinc	1 M KNO_3 and 0.9 M ammonia–ammonium salt buffer	Influence of V on an assembly with sinusoidal voltage in the range 100–200 V s^{-1}	130
Cadmium, thallium, copper and zinc	1 M CH_3COONH_4, 1 M acetate and ammonia–ammonium salt buffer	Study of the form of the reduction curves at an amalgamated silver electrode	131
Cadmium	1 M ammonia–ammonium salt buffer and Na_2SO_3	Rapid determination in the presence of copper	132
	Present together with lead and zinc in a 5000-fold excess of copper	Determination by differential oscillopolarography, resolving power ~30 mV	133
	Pure salts KCl, NH_4Cl, K_2SO_4, KI, KNO_3, KSCN, and $K_2C_2O_4$	Determination by an oscillopolarographic version of amalgam polarography with build-up	134
	Zinc electrolyte	Simultaneous determination of cadmium and nickel	135
Cadmium, lead, and zinc	4 M ammonia–ammonium salt buffer	Amperometric titration with Complexone III on an oscillopolarograph	136
Lead	1 M NH_4Cl	Selection of optimal conditions for analysis	129
Lead	1 M KNO_3 in the presence of atmospheric oxygen, buffer solutions	Influence of V on ΔE_{pak}; change to irreversible reaction with increase in pH; two forms of ion in solution $PbOH^+$ and $HPbO_2^-$	130
	Lead in bismuth without removal of O_2	Bismuth does not interfere in the determination of lead as far as a ratio Pb : Bi = 1 : 300	137
Bismuth and lead	Lead and bismuth in copper-based alloys	Determination of small quantities	138
Lead	In sea water and the basic rocks of the Pacific volcanic belt	Determination of small quantities	139,140
	In titanozirconate ceramic	Determination of small quantities	141
	In water, petrol, and biological materials	Determination by differential oscillopolarography	142
Lead	In blood	To 0.1 γ in 20 ml solution	143

Table cont'd.

Ion	Materials studied and conditions of polarography study	Results obtained	Refs
1	2	3	4
Thallium	In the presence of atmospheric oxygen, cobalt, and manganese	Quantitative determination	144
Fe^{3+}/Fe^{2+}	0.4 M H_2SO_4	Influence of V on the form of the curves at a Pt electrode	145
	Pyrophosphates in the presence of titanium and copper	Quantitative determination	146
Fe^{2+}	Mixed complexes with bipyridyl and phenanthroline and acetonitrile	Determination of adsorption-kinetic factors in electrolytic reduction	147
	Sulphuric acid medium	New method of coulometric study at Pt and Au electrodes down to ~10^{-7} M	148
Copper and antimony	In the presence of bismuth, cadmium, lead and zinc	Determination of down to 10^{-6} M by difference oscillopolarography	15
Zinc	In the presence of a 290-fold excess of nickel, 690-fold excess of cadmium, and 3580-fold excess of copper	Determination of down to ~3×10^{-6} M by difference oscillopolarography	15
Antimony	1 M HCl	Oscillopolarographic characteristics of the reduction	87
	In cast iron, 6 M HCl	Quantitative determination	149
	6 M HCl	Traces down to 0.1 γ in 1 ml	150
Bismuth	Semiconducting alloys, potassium chloride and oxalic acid in the presence of a 100-fold excess of tin	Quantitative determination	151
Copper and lead	In the presence of sulphonic acid derivatives of 8-quinolinol	Determination of down to 0.013 γ and 0.2 γ in 1 ml respectively	152
Cobalt and nickel	In nickel and cobalt	Quantitative determination	153
Nickel	In cobalt salts, saturated $CaCl_2$ solution without removal of O_2	Quantitative determination	154
Nickel, cobalt, zinc	Pyrophosphate background	Selection of conditions for analysis	155,156
Aluminium	In thorium compounds, in the complex with 2,2,4-trihydroxyazobenzene-5-sulphonic acid	Quantitative determination of down to fractions of 1 γ	157
	In solutions of complex-forming salts	Oscillographic behaviour	158,159
Copper, silver, gold	In the presence of chlorides, thiocyanates, ammonia, pyridine, ethylamine, 2-aminoethanol, 2,2'-2"-nitrilotri(ethanol), piperidine and ethylenediamine	Study of complex formation and selection of conditions of analysis	160
Palladium, copper, gold	In alloys	Quantitative determination	160
Gold, silver	In gold coatings on molybdenum and tungsten, in plant ash, in pure antimony	Determination of ultra-small quantities with preliminary concentration at a carbon paste electrode	161,163
Palladium	In the presence of a 70-fold excess of copper	Quantitative determination	162
Ruthenium, rhodium, palladium, osmium, iridium	In solutions of chloride, thiocyanates, cyanides, ammonia, and pyridine	Study of the electrolytic reduction of complexes, selection of conditions for the analysis of ruthenium, rhodium, and palladium in alloys	164
Niobium	In titanozirconate ceramic, in titanium–niobium and tantalum–niobium alloys, 23 N H_2SO_4	Quantitative determination	141,165, 166
Titanium	In titanozirconate ceramic, in sodium pyrophosphate solution, in the presence of uranium, in phosphoric acid media	Quantitative determination	141,167, 56,168

Table cont'd.

Ion	Materials studied and conditions of polarographic study	Results obtained	Refs
1	2	3	4
Uranium, molybdenum	In the presence of a 10-fold excess of Ferron (7-iodo-8-quinolinol-5-sulphonic acid)	Simultaneous quantitative determination	169
Vanadium	Mineral acids, ammonia-ammonium salt buffer	Study of the multi-stage nature of the reduction $V^{V} \rightarrow V^{II}$; separate stages almost reversible	130,170
Tungsten	7 M hydrochloric acid	Selection of conditions for analysis, use of second peak for reduction of tungstate anion	171
ReO_4^-, $ReCl_6^{2-}$	1-11 M hydrochloric acid	Study of stepwise reduction	172-174
Europium, ytterbium	Monazite sand, background containing ammonium salts and hydrazine	Study of the influence of the composition of the background on the form of the curves, quantitative determination	175
Samarium, dysprosium, ytterbium, lutetium, lanthanum, praseodymium, terbium	Various mineral acids, lithium chloride	Determination of the pH of the start of precipitation of the hydroxides, oscillopolarographic characteristics of the reduction, quantitative determination in phosphors	176-185
Scandium	Lithium chloride acidified with hydrochloric acid	Irreversible reduction at Au, Ag, Ni electrodes, scandium discharge peak follows hydrogen ion discharge	186
Germanium	In solutions of halides, sulphates, carbonates, phosphates	Quantitative determination of Ge^{IV} in 1 M NH_4Cl in the presence of Complexone III	188
	Semiconducting materials, in the presence of selenium, tin, and zinc, alkali solutions with pH ~12 in the presence of oxalate anions	Quantitative determination	189-191
Gallium	Semiconducting alloy, 0.2 M alcoholic solution of tetraethylammonium iodide	Quantitative determination of tenths of 1% gallium	192
Tellurium	Hydrochloric and sulphuric acids	Oscillopolarographic characteristics of reduction, second peak used for analysis, 100 times greater than first	193
Uranium	Concentrated phosphoric acid	Determination of down to $\sim 4 \times 10^{-7}$ M	194
Oxygen	In aqueous solutions, in petrol	Study of oscillopolarographic behaviour, quantitative determination	195,196
Boron	B-Si-C alloys, in a solution of orthoboric acid, sodium sulphite, and mannitol	Determination as mannitol-boric acid	197
Sulphur	In petroleum products, background of 0.04 M sulphuric acid in ethanol	Quantitative determination of aggressive sulphur (S and H_2S) at flowing mercury and Ag electrodes	198
Halogens	In solutions of potassium halides and nitrate	Quantitative determination at an Ag electrode	199
Sulphur, arsenic, and phosphorus anions	Neutral salts and alkaline solutions	Study of oscillographic behaviour, selection of conditions for direct and indirect determination	200-203

The material presented has dealt with the study of various elements in solution. In combination with solid electrodes, however, the method of oscillographic polarography has also been used to study salt melts [204-207]. Silver, lead, and cadmium chlorides have been studied in an equimolar mixture of potassium and sodium chlorides in the range 700-900° [207]; the results confirmed the earlier conclusion [205] that oscillographic polarography can be used for rapid quantitative analysis in molten salts.

The reduction of silver ions in an LiCl-KCl eutectic melt at 500° at low rates of application of the voltage at a platinum cathode [205], and the behaviour of cadmium, lead, tin, and copper ions in an $AlCl_3$-NaCl melt in the range 150-230° at a d.m.e. [208] have also been studied. The behaviour of halide anions was studied in a molten sodium nitrate-potassium nitrate eutectic with stationary and dropping mercury electrodes in the range 230-270° [209]. It was shown that in spite of the fact that the products of the oxidation of these anions at the electrode react with nitrates, distorting the form of the oscillopolarograms, their quantitative determination in the melts is possible.

2. Analysis of Organic Compounds

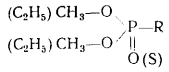
By means of classical polarography it is possible in principle to determine ~10% of all organic substances containing a polarographically active group in the molecule, whereas by means of oscillographic polarography it is possible to analyse not only these compounds but also those which in solution alter the capacity of the electrode double layer. As with inorganic materials, most papers on organic oscillopolarography have been devoted to the study of the behaviour of compounds under different conditions, the influence of the latter on the form of the oscillopolarograms, and the development, on the basis of these results, of specific methods of analysis.

Among organic compounds containing a nitrogen atom in the molecule, detailed studies have been made of the irreversible oxidation of a number of primary, secondary, and tertiary aliphatic amines at a platinum electrode in acetonitrile in a background of $NaClO_4$ [210]. The difficulty of oxidation increases on going from tertiary to secondary and primary amines. Oscillographic studies at a d.m.e. have also been made for hydrazine and hydroxylamine in alkali solutions [211]; the results, however, did not make it possible to reach an unambiguous conclusion regarding the nature of their anodic peaks; they are associated either with oxidation of the substance at the electrode or with reaction with mercury.

Detailed studies have been made of organic compounds containing sulphur, in particular thiourea and its derivatives [52,212], and various thiols [53,213]. The oscillograms for thioacetamide, thiourea, diphenylthiourea, thiosemicarbazide, and dithizone give a sharp cathodic peak, with adsorption characteristics, over a wide pH range. Its height depends not only on the concentration of depolariser, but also on the initial potential of polarisation of the mercury electrode, since it is associated with the formation of a film of an intermediate compound of thiourea or its derivative with mercury. This intermediate compound is capable of undergoing hydrolysis with the formation of mercury sulphide, corresponding to the same cathodic peak on the oscillopolarograms. A peak with analogous form and properties was also observed on the oscillopolarograms of thiols: thioglycollic and thioacetic acids, sodium thioglycollate, cysteine, etc. [53,213,214]. Various S-methyl-substituted thioureas in alkaline solution also gave a cathodic peak similar to the thiol peak [52]. The latter is due to the reduction of mercury thiolate, produced by the reaction of the thiols with mercury on the electrode surface. The works cited [213,214] also describe the oscillopolarographic behaviour of substances containing thiol and thione groups simultaneously in the molecule, such as sodium diethyldithiocarbamate, K ethyl xanthate, and di-isopropyl xanthate disulphide. Their behaviour in alkaline and acidic media resembles that of thiourea and its N-substituted derivatives. Almost no differences are observed in the form of the curves for K ethyl xanthate

and sodium diethyldithiocarbamate in acid solutions, since under these conditions the compounds decompose with the formation of carbon disulphide, which is responsible for the electrochemical activity of the polarographic solution. The works cited[52,53,212-214] consider the possibility of using oscillographic polarography to determine the following organic compounds in their mixtures with one another: thioglycollic acid and thiourea, K ethyl xanthate and sodium diethyldithiocarbamate, and K ethyl xanthate and carbon disulphide, in strongly alkaline or acidic solutions.

As noted above, many organic substances are not reduced or oxidised, but nevertheless give sharp peaks on the oscillopolarograms, due to a sharp change in the capacity of the electrode. Peaks of this kind were found to be characteristic of most organophosphorus compounds used as insecticides, and can be used for quantitative determinations at concentrations of 3×10^{-7} M [215]. The work cited[215] describes a study of dimethyl and diethyl esters of phosphoric and thiophosphoric acids with the general formula



where R represents various alkyl, aryl, or mixed substituents, in a medium of water and organic solvent (CH_3OH, C_2H_5OH, and CH_3COCH_3) in the ratio 1 : 1, with 0.2 M HCl, KCl, or NaOH solutions as background. It was noted that the peaks on the curves are more stable with time for the thio-analogues than for the phosphates and more stable in HCl or KCl than in alkali.

The behaviour under the conditions of oscillographic polarography has been studied for the semicarbazones and thiosemicarbazones of carbonyl compounds[216], the phenylhydrazones of pyruvic aldehyde and ethyl diketobutyrate[217], 5-nitromucic acid and its methyl ester[218], various compounds containing nitro and azomethine groups in the molecule[64], the azo dye Eriochrome Black[219], nitro- and aminoterephthalates[220], the nitriles of acrylic, vinylacrylic, and cinnamic acids[105], the organic analytical reagents 1-nitroso-2-naphthol[221], disodium 1-nitroso-2-naphthol-3,6-disulphonate[222], Cupferron[107], and various heterocyclic compounds: indolizines[223], aminobenzothiazoles[224-226], pyrazine[227], derivatives of 4,4-bis(triansylamino)stilbene-2,2-disulphonic acid[228], and pyrimidones[229].

The study of the behaviour of organic substances under the conditions of oscillographic polarography, described in Refs. 216, 218, and 227, and more particularly Ref. 64, has shown that the form of the curves for organic depolarisers in general depends on their concentration, the pH of the solution, the nature of the solvent, and the concentration of the background electrolyte. The fact that the form of the oscillopolarograms depends on the conditions of the polarographic study and the concentration of the depolariser, which is not always known in analysis, casts doubt on the effectiveness of the use of the so-called oscillopolarographic atlas for the identification of organic substances. This atlas[230] was based on the assumption that the form of the oscillopolarogram is specific for a given substance or series of structurally related substances, and has been proposed for the qualitative detection of organic depolarisers.

Oscillographic polarography has also been used for quantitative determinations in the analysis of α,β-unsaturated ketones present in technical methyl isobutyl ketone[231], various substances exhibiting the properties of photographic developers, such as hydroquinone, *p*-aminophenol[232,233], phenidone[233], substances acting as sensitisers[234,235], and tetraethylthiuram disulphide in the presence of elementary sulphur in organic extracts[236]. Various versions of the use of one-pulse and multi-pulse oscillographic polarography for the analysis of developers, stabilisers, and colour developer components in photography, and polyethylene glycols, which are chemical stabilisers in the production of cinephotographic materials, have been discussed[234]. In the last example an empirical relationship was established between the surface activity of the substance, and hence the height of the adsorption–desorption peaks on the oscillopolarograms, and the molecular weight of the polyethylene glycols.

A study of the oscillographic behaviour of various organic dibasic acids with the general formula $HOOC-(CH_2)n-COOH$, where $n = 0, 1, 2, 3$, or 4, showed that acids such as oxalic, malonic, succinic, and adipic in a background of $NaClO_4$ in the presence of Ge ions give distinct reduction peaks on the oscillopolarograms. Germanium itself is inactive in weakly acidic media, and its presence does not interfere in the analysis, but on the contrary increases the height of the peak for the dicarboxylic acid as a consequence of its catalytic action on discharge at the electrode.

The heights of the peaks depend on the concentration of catalyst depolarisers, the buffer capacity and acidity of the solution, and the nature of the indifferent electrolyte. It was found that with increase in the number of CH_2 groups in the organic acid molecule in the series malonic–succinic–adipic there is a gradual decrease in the catalytic peak and its potential is displaced towards more negative values[237].

Oscillographic polarography has been used successfully for the quantitative analysis of the three stereoisomeric forms of 1,4-distyrylbenzene in the presence of one another[238]. On classical polarograms these stereoisomers give waves with similar values for the half-wave potentials. If the differential oscillopolarograms are recorded, however, the selective determination of the *cis-cis* and *cis-trans* isomers in the mixture becomes possible (the *trans-trans* isomer is separated as a consequence of its low solubility in the polarographic medium) with the condition that the relative concentration of the *cis-cis* form does not exceed 75–80%.

It should be noted that the analysis of organic compounds by oscillographic polarography exhibits a number of specific features, which have been partly discussed above. The adsorbability of the depolariser species on the electrode surface explains the production of two components of the reduction current—the surface component (sharp peak) and the volume component (with a diffusion loop)[64,117]. Since oscillographic polarography exhibits a fairly high resolving power with respect to potentials (this increases for processes involving the adsorption of depolariser species), the form of the curves in the last instance can lead to the erroneous conclusion that the solution contains two electro-active substances. These characteristic features of the behaviour of organic substances under the conditions of oscillographic polarography must be taken into account in the development of analytical methods involving its use.

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The development of modern radioelectronics has made it possible to create a wide range of new techniques

in oscillographic polarography, and these have greatly extended the range of practical applications of the method.

It should be noted, however, that each of the methods has its disadvantages and limitations[4]. Those methods which provide promising possibilities in analytical chemistry are particularly noteworthy. These are primarily the method involving fractional differentiation of the oscillopolarographic curve, which makes it possible to eliminate intermediate diffusion components, and hence to alter its form in appropriate fashion; the method involving automatic and controlled compensation of the volume resistance of the solution, which makes possible the polarographic study of non-aqueous solutions; and the method involving a stepped polarising voltage, which eliminates the influence of the background current. It should be noted that oscillographic polarography with triangular scanning of the voltage has a definite advantage over the method involving a saw-toothed form of polarising voltage, since it makes it possible to obtain information on the cathodic and anodic processes simultaneously.

The main achievements of oscillographic polarography are associated not only with the development of new methods of measurement. The development of methods for increasing the sensitivity, based on the adsorption of depolariser species, the action of various salting-out agents, or other means of concentrating the substance being determined on the electrode surface shows that the possibilities provided by oscillopolarography are not yet exhausted. The importance of studying the various factors which determine the form of the oscillographic polarograms and which must be taken into account in the qualitative and quantitative analysis of solutions should also be noted.

Review of published work shows that oscillographic polarography can be used successfully to study electrochemical processes complicated by fast chemical reactions taking place together with transfer of electrons to the depolariser. The interpretation of the oscillopolarograms obtained for this purpose for organic compounds which can be adsorbed on the electrode surface is complicated, however, and further work in this direction is required.

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Nature of Carbon-Halogen Bonds

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This paper is a critical review of the literature on the problem of the nature of carbon-halogen bonds. It examines the various physical properties of halogen-containing organic compounds which are useful in discussing the problem of the chemical bond (infrared spectra, dipole moments, interatomic distances, nuclear quadrupole interaction constants, nuclear magnetic resonance). Special attention is paid to results from nuclear magnetic resonance, which show the uselessness of treating the properties of organohalogen compounds from the position of mesomerism-resonance theory. The correlation between the chemical shifts of nuclear magnetic resonance and the σ-constants of the substituents in various organohalogen compounds is considered. Attention is paid to the hybridisation of the orbitals of the carbon and halogen atoms and to the associated electronic displacements in unsaturated and aromatic systems. 85 references.

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I. INTRODUCTION

In the interpretation of the properties of molecules contemporary theories of organic chemistry employ ideas about the displacement of valence electrons by induction and conjugation mechanisms. Initially it was thought that the conjugative displacement of electrons, that is, their displacement from one bond to another, can occur in a molecule under the influence of a reagent (Robinson, Lowry, 1922–1923). It was proposed to represent graphically the effect of polarisation according to this mechanism by using curved arrows, symbolising the transfer of electrons from the octet of one atom to the octet of another. It was subsequently postulated that a state of constant polarisation by the conjugative mechanism also occurs in a non-reacting molecule (Arndt, 1924; Ingold, 1926). This conception, now known under the name of the theory of mesomerism, was subsequently used, mostly by Ingold, to explain a large number of problems in the reactivity of organic compounds. The use of quantum-mechanical calculations on unsaturated and aromatic systems using the π-electron approximation (Hückel, Pauling, 1932) was a further development of ideas on the delocalisation of valence electrons in organic molecules. To describe the electronic displacements in complex molecules which contain, in particular, hetero-atoms, the theory of resonance employs a set of structures corresponding to the limiting states of electron displacement

according to the conjugative mechanism. In this approach to the description of the electronic structure of a molecule the resonance theory becomes an adequate theory of mesomerism, differing only from the latter in the manner of representation of the electronic displacements that can be postulated.

The theory of mesomerism–resonance, or, as it is still called, the theory of conjugation (translated into Russian as teoriya sopryazheniya) has now received almost universal acknowledgement and is widely employed in dealing with the physical and chemical properties of organic compounds. Nevertheless, detailed examination shows the mesomerism–resonance theory to be in conflict with many experimental results. The most striking and convincing deficiency of this theory is in its application to organohalogen compounds, the properties of which have been thoroughly studied by physical and chemical methods and which also are the subject of detailed consideration from the standpoint of the theory of mesomerism.

We will consider below some physical properties of halogen derivatives of hydrocarbons—infrared spectra, dipole moments, interatomic distances, nuclear quadrupole resonance (NQR) constants—which are usually produced in support of the carbon–halogen bond's having partial double bond character. As will become evident from what is stated below, to explain some of the physical properties of the halogen derivatives of unsaturated and aromatic hydrocarbons it is unnecessary to have resort to mesomerism–resonance theory, since these properties can be substantially explained by the theory of the hybridisation of the orbitals of the carbon and halogen atoms and other physical criteria of the chemical bond, namely the NQR constants, are direct proof that the halogen atoms exhibit hardly any mesomeric effect. From the experimental results on the NQR constants it can be shown that the bonding orbitals of the halogen atoms in various types of halogen derivatives of hydrocarbons differ in their degree of hybridisation.

The increased strength of the carbon–halogen bond and the lower chemical lability of the halogen in a halogenobenzene as compared with an alkyl halide is explained by the greater overlap of the single-electron orbitals of the carbon and halogen exhibited in the aromatic compound with a higher *s*-character, and not by a greater number of electrons localised on the C–Hal bond in the aromatic compound (as is assumed in the mesomerism–resonance theory). The concept of the mesomerism theory of the participation of a conjugation mechanism in the transmission of the influence of the halogen atoms on the distribution of electronic charges in unsaturated and aromatic systems and the treatment (based upon this mechanism) of the reactivity of halogen-containing organic compounds are worthless.

2. ENERGETICS OF THE MESOMERIC STATE

Ingold originally assumed[1] that "in the halogen series, iodine, being the most capable of deformation, should exhibit the greatest tendency towards an increase in its covalency" and arranged the halogens in the following series according to decreasing mesomeric effect:

$$I > Br > Cl > F. \qquad (1)$$

Such a sequence of intensities in the displacement of electrons under the influence of the +M effect agrees with the order of the halogens according to their decreasing ability to withdraw electrons under the influence of the inductive (*I*) effect and hence leads solely to an increase in the difference between the electronegativities of the halogen atoms. Naturally, the attraction of ideas about the mesomeric effect for halogens, in the stated succession of its appearance, could not prove to be helpful for the interpretation of the physical and chemical properties of halogen-containing organic compounds. Progress in this respect would necessitate a system of effects opposite in their action, a system which would allow the difference between the atoms to be obliterated to the extent to which this is necessary for the interpretation of the experimental facts. Consequently, Ingold subsequently arranged the halogens according to their ability to increase the covalency in the reverse order:

$$F > Cl > Br > I, \qquad (2)$$

in which the mesomeric effect appears most strongly with fluorine and least with iodine. However, there is no physical basis for this series of decreasing mesomeric effects for the halogens, since it does not agree with the ionisation potentials, which increase from iodine to fluorine and not in the opposite direction.

To explain this contradiction it was assumed that the tendency towards an increase in covalency is determined not by the ionisation potentials of lone pairs but by the degree of overlap of the atomic orbitals which is the greater the less the atoms which form the double bond differ in size[2,3]. The worthlessness of this explanation becomes clear on examining actual data. The difference between the energies of double bonds formed by different atoms is ~ 10–50 kcal mole^{-1}.[4] Furthermore, the ionisation potentials of the electrons in the $tr^2tr^2tr\pi^2$ valence state of the halogens (as follows from the results on the energies of the ground states and the energies for promoting to the valence states[5,6]) for F, Cl, Br, and I are 18.24, 13.73, 12.37, and 10.88 eV respectively, that is, the difference in the ionisation potentials of the π-electrons of fluorine and chlorine is 104 kcal mole^{-1} and of fluorine and iodine is 170 kcal mole^{-1}. From energetic considerations, clearly if halogen atoms are capable of showing a mesomeric effect it should decrease in the order I > Br > Cl > F, but then its role as a working instrument in the treatment of the physical parameters of carbon–halogen bonds and of the chemical properties of halogen-containing organic compounds is lost.

3. INFRARED SPECTRA

Results on the vibrational frequencies of the C=C bond in halogenoethylenes will be examined for proof that a mesomeric effect is produced by halogen atoms. The position of the vibrations for this bond in chloroethylene (1608 cm^{-1}), bromoethylene (1598 cm^{-1}), and iodoethylene (1581 cm^{-1}) compared with that of the frequency of the vibration in ethylene (1621 cm^{-1}) is explained by the influence of resonance structure $\bar{C}H_2-CH=\overset{+}{X}$ with an ordinary C–C bond[7].

If the reduction in the vibrational frequencies were connected with the influence of the mesomeric effect of the halogens, then a reduction in the frequency of the vibrations of the C=C bond in fluoroethylene would also be expected, but for this compound the wavenumber is 1650 cm^{-1},[8] that is, higher than for ethylene. Undoubtedly the reduction in the vibrational frequencies for chloro-, bromo-, and iodo-ethylene is due to mechanical reasons—the replacement of hydrogen atoms by the heavy halogen atoms. When the alkene molecule is sufficiently large, the introduction of a chlorine atom has no effect on the vibrational

frequency of the C=C bond. Thus the wavenumbers for tetraethylmethylene [2,3-dimethylbut-2-ene] and trimethylchloroethylene [2-chloro-3-methylbut-2-ene] are the same (1672 cm^{-1}).

4. DIPOLE MOMENTS

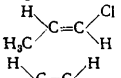
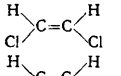
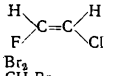
There is a body of opinion that results on dipole moments provide experimental proof of the mesomeric effect of halogens [2,3,9]. That the dipole moments of the halogenobenzenes are lower than those of the methyl halides is explained by the effect of the mesomeric structures:

in that the difference in the dipole moments of the aliphatic and aromatic series $\mu CH_3X - \mu C_6H_5X$, is regarded as a measure of the mesomeric effect. This is illustrated by Table 1 (columns 2, 3, and 4), data taken from Coulson's book [9].

Table 1.

x	F	Cl	Br	F	Cl	Br
1	2	3	4	5	6	7
μ (CH_3X)	1.81	1.87	1.80	1.79	1.87	1.80
μ (C_6H_5X)	1.58	1.72	1.77	1.61	1.69	1.64
μ (CH_3X) — μ (C_6H_5X)	0.23	0.15	0.03	0.18	0.18	0.16

Table 2.

Compound	U_p	s-nature of carbon	x_C, eV	s-nature of halogen	x_{Hal}, eV	i	References on molecular structure and U_p	Notes
Cl_2	0.99	—	—	0.01	9.48	—	20.21	
CH_3Cl	0.68	0.220	7.81	0.20	11.35	0.15	22.21	
CF_3Cl	0.71	0.274	8.31	0.19	11.25	0.12	23.21	
CH_2Cl_2	0.70	0.228	7.89	0.19	11.25	0.14	24.25	$\angle HCH=112°$
C_6H_5Cl	0.65	0.333	8.79	0.26	11.94	0.13	26	$\angle C_2C_1C_6=120°$
$CH{\equiv}CCl$	0.726	0.500	10.38	0.24	11.75	0.05	27.21	
CH_2CHCl	0.64	0.280	8.36	0.25	11.84	0.14	28	
	0.65	0.325	8.77	0.25	11.84	0.13	29	
	0.66	0.285	8.41	0.24	11.75	0.14	30	
	0.67	0.285	8.41	0.23	11.65	0.13	31	
Br_2	0.99	—	—	0.01	8.50	—	20.21	
CH_3Br	0.75	0.202	7.65	0.17	10.08	0.11	22.21	
CF_3Br	0.80	0.274	8.31	0.14	9.79	0.07	32	$\angle FCF=108.6$
C_6H_5Br	0.74	0.333	8.79	0.21	10.47	0.06	33	
$CH_3C{\equiv}CBr$	0.84	0.500	10.38	0.17	10.08	0.01	34	
$CH_2{=}CHBr$	0.72	0.333	8.79	0.22	10.57	0.08	35	
I_2	0.94	—	—	0.06	8.55	0	20.21	
CH_3I	0.84	0.196	7.59	0.10	8.86	0.06	22.21	
$CH_3C{\equiv}CI$	0.97	0.500	10.38	0.10	8.86	0.07	34	
$CH_2{=}CHI$	0.82	0.332	8.84	0.16	9.31	0.02	20.36	

However, the dipole moments cannot serve as confirmation of the existence of a mesomeric effect for the halogens. The lower dipole moments of the halogenobenzenes is explained by the carbon atoms in the trigonal valence state (sp^2) exhibiting a higher electronegativity owing to which the polarisation of the C_{sp^2}–Hal bond is less than that of the C_{sp^3}–Hal bond. The effect of the hybridisation of the carbon orbitals on the moments of the C–Hal bond was examined by Petro [10]. Thus, the moment of the C_{sp^3}–F bond is 1.50 D, that of the C_{sp^2}–F bond is 0.95 D, that of the C_{sp^3}–Cl, C_{sp^2}–Cl, and C_{sp}–Cl bonds are 1.56, 1.07, and 0.61 D respectively, and those of the C_{sp^3}–Br and C_{sp^2}–Br bonds 1.49 and 1.01 D. The dipole moments of the halogenohydrocarbons also show the effect of the orbital hybridisation of the halogen atoms which is reflected by the electronegativities of their bonding orbitals (see Table 2). As regards the values of $\mu(CH_3X) - \mu(C_6H_5X)$, on selecting the most reliable values of the dipole moments [11] this difference disappears (Table 1, columns 5, 6, and 7).

In the CH_3X and $CH_2{=}CHX$ series the differences in the dipole moments for the fluoro-, chloro-, and bromo-derivatives are 0.36, 0.42, and 0.41 D respectively; for CH_3X and $CH{\equiv}CX$ this difference increases from fluorine to bromine (1.04, 1.43, and 1.80 D respectively) [11].

5. HYBRIDISATION OF THE ORBITALS OF HALOGEN ATOMS AND LENGTHS OF THE CARBON–HALOGEN BONDS

One of the main arguments in support of the halogen atoms exerting a mesomeric effect was the lengths of the carbon–halogen bonds in halogenohydrocarbons. Thus the shortening of the C–Cl bond in chlorobenzene and the chloroethylenes by 0.06–0.08 Å in comparison with the length of this bond in the halogenomethanes was explained by the presence of 15–18% double-bond character [12]; in the halogenoacetylenes, where the shortening of the carbon–halogen bond reaches ~ 0.15 Å, the degree of double-bond character is estimated at 30–36%. [13]

In the light of the theory of hybridisation, variations in the lengths of the carbon–halogen bonds are explained by orbital effects—the sizes of the covalent radii of carbon and the halogens in various valence states, realisable in one molecule or another [14]. The hybridisation of the orbitals of carbon atoms is determined simply from results on the geometry of the molecules [15]. Information about the hybridisation of the bonding orbitals of halogen atoms is underlined by the nuclear quadrupole interaction constants. The use of the latter for determining the degree of hybridisation of the orbitals of halogen atoms was hindered by the fact that they are functions of both the degree of hybridisation (s) and the ionicity of the bond (i). Both these parameters have a definite relation with a single experimental quantity, the number of non-bonded p-electrons [sic]:

$$U_p = -\frac{eQq_{mol}}{eQq_p},$$

in accordance with Eqn. (5):

$$U_p = (1-s)(1-i). \qquad (5)$$

Various attempts [16,17] were made earlier to find a relation between the ionic nature of a bond and the difference in electronegativities of the bound atoms, in order to substitute the ionicity of the bond in Eqn. (5) to determine the degree of hybridisation of the halogen orbitals. In this, however, no account was taken of the extremely important fact that a change in the hybridisation of the orbitals of the halogen atom is accompanied by a change in its electronegativity. After Hinze and Jaffe [5,6] had found a relation between these two parameters it was possible to determine the s-nature of the halogen orbitals and to show its effect on the length of the carbon–halogen bonds [14].

The ionic nature of a bond i is determined on the basis of the concept of bond electronegativity with the aid of Eqn. (6):[18]

$$i = |nAj - 1| = \left| \frac{\Delta\chi}{2(C_A + C_B)} \right|, \quad (6)$$

where nAj is the number of electrons in the jth orbital of atom A, $\Delta\chi$ the difference between the electronegativities of atoms A and B, eV; C_A and C_B the half-differences between the ionisation potential and the electron affinity for the orbitals of atoms A and B respectively, $C = \frac{1}{2}(I_V - E_V)$. The electronegativity of the carbon and halogen atoms depends linearly on the s-character of the bonding orbital[5], as does the ionisation potential I_V and the electron affinity E_V for the halogens. The ionisation potentials and electron affinities of the carbon atoms in a state of non-integral hybridisation are found from curves constructed from available information for sp^3, sp^2, and sp states. The valence states of the carbon atoms (s-nature) are found from results on molecular structure with the aid of the relation derived by Coulson[19]. Subsequently by selecting the values of i which satisfy the experimental results about the number of non-bonded p-electrons (5) the s-nature of the halogen bonding orbitals was calculated. To determine the degree of hybridisation of the halogen orbitals in bromo(methyl)acetylene and iodo(methyl)acetylene [1-bromo- and 1-iodo-propyne], in which the electronegativity of the halogen is less than for carbon in the sp state, Eqn. (7) is used[16]:

$$U_p = (1 - s)[1 + i(1 + 2C)] \quad (7)$$

where C is a screening constant, 0.13 for bromine and 0.12 for iodine.

The calculated values of the s-nature of the halogen orbitals in various types of halogenohydrocarbons are given in Table 2, which shows that the bonding orbitals of chlorine are 19–26% hybridised, those of bromine 14–21%, and those of iodine 10–16%.

In the analysis of results on the interatomic distances it is noteworthy that in different types of halogenohydrocarbons the carbon atoms in different valence states have different covalent radii[14,15]. A significant part is also played by the change in the covalent nature of the halogen with change in the covalent radii of the carbon and halogen in one or another valence state depending on the ionicity of the bond. Conclusions about the degree of double-bond character can only be drawn from the lengths of the carbon–halogen bonds if all these factors are taken into account.

The covalent radii of carbon, as a function of the s-nature of its orbital (r_C^{cov}), and their change with the ionicity of the bond (Δr_C) are determined by the relations (8) and (9) derived earlier[15]:

$$r_C^{cov} = (0.854 - 0.328)\,\text{Å}, \quad (8)$$

$$\Delta r_C = 0.88\,|n_C - 1|\,\text{Å}, \quad (9)$$

where n_C is the number of localised electrons in the carbon orbital.

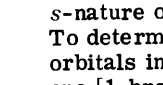
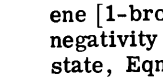
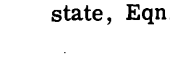
The variation of the covalent radius of chlorine with the s-nature of its bonding orbitals and its change with the ionicity of the bond are determined by starting from results for chlorotrifluoromethane and dichloromethane, in which the s-nature of the chlorine orbitals is the same (0.19) (see Table 2). By using the results on the s-nature of the carbon orbitals and the bond ionicity i in these halogenomethanes (Table 2), by use of Eqns. (8) and (9) the covalent radii $r_C^{*\delta}$ can be found, and subtraction of these from the interatomic distances gives the covalent radii of chlorine $r_{Cl}^{-\delta}$ for CF_3Cl and CH_2Cl_2 (Table 3). From the values of $r_{Cl}^{-\delta}$ and i for these molecules can be found the covalent radius of chlorine for its hybridisation (0.934 Å) and ΔrCl, Eqn. (10), and then by bearing in mind that for the chlorine molecule the s-character is 0.01 and r_{Cl}^{cov} = 0.994 Å, the relation between the covalent radius of chlorine and the degree of hybridisation of its orbital, (11), can be found:

$$\Delta r_{Cl} = 1.30\,|n_{Cl} - 1|\,\text{Å}, \quad (10)$$

$$r_{Cl}^{cov} = (0.997 - 0.33\,s)\,\text{Å}. \quad (11)$$

[There is no Eqn. (12) in this paper (Ed. of Translation)].

Table 3.

Compound	r_C^{δ}	r_{Hal}^{δ}	d (C–Hal) calc.	d (C–Hal) published results
CH_3Cl	0.650	1.126	1.776	1.781[0a]
CF_3Cl	0.658	1.090	1.748	1.748[32]
CH_2Cl_2	0.656	1.116	1.772	1.772[33]
C_6H_5Cl	0.631	1.080	1.711	1.712[34]
$CH{\equiv}CCl$	0.646	0.983	1.629	1.632[27]
$CH_2{=}CHCl$	0.639	1.096	1.735	1.726[35] 1.736 ± 0.01[36]
	0.633	1.083	1.716	1.728[35]
	0.638	1.100	1.738	1.724[36]
	0.647	1.090	1.737	1.726[31]
CH_3Br	0.691	1.248	1.939	1.939[38]
CF_3Br	0.702	1.202	1.904	1.919[39]
C_6H_5Br	0.683	1.186	1.869	1.867[43]
$CH_2C{\equiv}CBr$	0.699	1.094	1.793	1.793[14]
$CH_2{=}CHBr$	0.675	1.195	1.870	1.853[35] 1.891[40]
CH_3I	0.737	1.402	2.139	2.139[38]
$CH_3C{\equiv}CI$	0.752	1.239	1.991	1.991[14]
$CH_2{=}CHI$	0.727	1.343	2.070	2.089[40]

The calculated lengths in CH_3Cl, chlorobenzene, and chloroacetylene, obtained with Eqns. (8)–(11) and the data of Table 2, agree well with experimental values (Table 3). The calculated length of the C–Cl bond in vinyl chloride differs from some of the experimental results[28] but agrees with others[20]; the differences between the calculated and experimental lengths of the C–Cl bond for 1-chloropropene, *cis*-1,2-dichloroethylene, and *cis*-2-chloro-1-fluoroethylene vary between +0.01 and −0.01 Å, attributable to the uncertainty in the structural parameters of these molecules.

The dependence of the covalent radius of bromine on the s-character of its orbitals, Eqn. (13), and the change in the orbital radius with the number of electrons localised on it, Eqn. (14) were calculated from results on CH_3Br, bromo(methyl)acetylene [1-bromopropyne] (with equal s-character of the halogen orbitals), and Br_2.

$$r_{Br}^{cov} = (1.144 - 0.23\,s)\,\text{Å}, \quad (13)$$

$$\Delta r_{Br} = 1.28 \cdot |n_{Br} - 1|\,\text{Å}. \quad (14)$$

The length of the C–Br bond in bromobenzene was calculated with the aid of Eqns. (8), (9), (13), and (14) and the data of Table 2, and differed from the experimental value by 0.002 Å. For CF_3Br the difference was 0.015 Å, which shows that the C–F bonds in this compound are of the "banana" type. The calculated value of the length of the C–Br bond in bromoethylene differs from the

experimental values (which show considerable variation) obtained from microwave spectra (1.853 and 1.891 Å).

The following relations for r_I^{cov}, Eqn. (15), and Δr_I Eqn. (16), were found from the results for CH_3I, iodomethyl)acetylene, and I_2.

$$r_I^{cov} = (1.342 - 0.15\,s)\,\text{Å}, \quad (15)$$

$$\Delta r_I = 1.25\,|n_I - 1|\,\text{Å}. \quad (16)$$

Starting from the parameters of the molecular structure adopted in work on iodoethylene [36] ($\angle C_2C_1I = 122.4°$, $\angle C_2C_1H = 120°$), the calculated length of the C–I bond is 0.019 Å shorter than that found. It is noteworthy that to calculate the length of the C–Hal bond in halogenoethylenes it is necessary to know $\angle C_2C_1H$, which was taken as 120° in work on bromoethylene and iodoethylene, The agreement of the calculated lengths of the C–I bond in iodoethylene with published data is obtained if $\angle C_2C_1H = 124°$.

Correlation equations (10) and (11) were derived from results for molecules (CF_3Cl and CH_2Cl_2) in which the mesomeric effect for chlorine should not appear. In chlorobenzene and chloroacetylene, where a mesomeric effect is theoretically possible the C–Cl interatomic distances would not obey Eqns. (10) and (11), should this effect appear, and the departure of the calculated values of the C–Cl bond lengths from the experimental ones would serve as a measure of the mesomeric effect of chlorine in aromatic and acetylene compounds.

At 5% double-bond character the length of the C–Cl bond in chlorobenzene would be shorter than that calculated by 0.021 Å, as follows from Eqn. (17):[12]

$$R = R_1 - (R_1 - R_2)\frac{3x}{2x+1}, \quad (17)$$

where R is the interatomic distance in a bond of intermediate type, R_1 the length of an ordinary bond, R_2 the length of a double bond, and x the degree of double-bond nature.

Actually the difference between the calculated and experimental lengths of the C–Cl bond in chlorobenzene is 0.001 Å.

Correlations establishing a relation between interatomic distances in carbon–halogen bonds and the hybridisation of the orbitals of the carbon and halogen atoms serves as proof of either the absence of a mesomeric effect for the halogen atoms or of its appearance to such a slight extent that it does not have any appreciable effect on the lengths of the carbon–halogen bonds.

6. NUCLEAR QUADRUPOLE RESONANCE

A most important and independent criterion of the ability of halogen atoms to show a mesomeric effect is provided by results on the nuclear quadrupole interaction, obtainable with the aid of microwave spectroscopy.

According to Goldstein and Bragg [37,38], a measure of the influence of the mesomeric effect in vinyl halides is provided by the asymmetry parameter, given by the expression:

$$\eta = \frac{\chi_{xx} - \chi_{yy}}{\chi_{zz}} \quad (18)$$

where χ_{xx}, χ_{yy}, and χ_{zz} are the quadrupole interaction constants along the corresponding coordinate axes x, y, and z, with χ_{zz} (eQq_{mol}) being the quadrupole coupling constant along the carbon–halogen bond. The degree of double-bond character of the carbon–halogen bond is determined by the quantity:

$$\delta = \frac{\eta \cdot eQq_{mol}}{^3/_2 eQq_{atom.}}, \quad (19)$$

and the percentage double-bond character = $100\,x\,\delta$.

The degree of double bond character has been calculated for various vinyl halides: 4–6% in vinyl chloride [28,38,39], 4% in *cis*-1,2-dichloroethylene [31], 4% in vinyl bromide [35], and 3% in vinyl iodide [36,39,40]. In evaluating the asymmetry parameter in the vinyl halides which are molecules of the asymmetric tap type, in which the principal axis of inertia does not lie along the direction of the carbon–halogen bond, a series of assumptions are made concerned with the impossibility of transforming the quadrupole interaction constants relative to the principal axes of the molecule a, b, and c into the new axes x, y, and z. In addition the values of the bond constants are very sensitive in relation to assumed parameters. Thus the experimental results are not inconsistent with the presence in vinyl chloride of only 2% double-bond character [28]. The difficulties in the calculation of χ_{xx} and χ_{zz} are due in particular to the insufficiently precise data about the molecular structure of the vinyl halides obtainable by electron diffraction.

The available information about the NQR in the halogen derivatives of benzene relates (except for bromobenzene) to the solid state. The quadrupole effects observed in these compounds, although distorted by the influence of the crystal field, show a very low degree of double-bond character in the carbon–halogen bond. Thus, in *p*-dichlorobenzene the double-bond character is 2.7 ± 0.7%, in *p*-chlorobenzyl chloride 2.4 ± 0.7%, in *p*-chloroaniline 2.0 ± 1%, [41] and in iodo-substituted benzenes the degree of double-bond character amounts to 1.6–2.8% (*m*-iodonitrobenzene 1.6%, *p*-iodoaniline 1.6%, *p*-di-iodobenzene 2.1%, 4-iodobenzoic acid 2.1%, 3-iodobenzoic acid 2.7%, *p*-iodonitrobenzene 2.8%) [42]. To obtain more reliable information about the degree of double-bond character of C_{sp^2}–halogen, Rosenthal and Dailey [33] made a fundamental investigation of the quadrupole effects in *gaseous* bromobenzene, in which (unlike the halogenoethylenes) the principal axis of inertia coincides with the direction of the carbon–halogen bond. It appeared that the quadrupole constants in the isotopic modification $C_6H_5{}^{79}Br$ agree with 1–2% double-bond character in the C–Br bond, and in the isotopic modification $C_6H_5{}^{81}Br$ there is no double-bond character, within the limits of accuracy of the measurements. The authors concluded that the explanation for the peculiarities of the C–Br bond in aromatic compounds in terms of the conjugation theory is implausible.

Hence modern results on the NQR spectra show either the complete absence of mesomeric effect for halogen atoms, or its appearance to such a slight extent that its influence should hardly be reflected in the physical parameters of the carbon–halogen bond and in the chemical properties of halogen-containing organic compounds.

7. NUCLEAR MAGNETIC RESONANCE AND CORRELATION OF THE CHEMICAL SHIFTS WITH THE σ-CONSTANTS OF THE SUBSTITUENTS

A discussion of the electronic structure of molecules often is based on a joint examination of NQR spectroscopic and chemical results and is greatly subject to the establishment and analysis of correlations between the ^{13}C, ^{1}H, and ^{19}F chemical shifts and the σ-constants of the substituents. This is quite regular, since the system of

inductive and mesomeric effects of the substituents, including halogen atoms, was developed on the basis of an examination of chemical properties. The dissociation constants of halogen-substituted phenylboric and benzoic acids, phenol, and aniline were the experimental material which stimulated Ingold to examine the problem of the relative intensity of the mesomeric effect at the halogens. As follows from the positive values of the substituent constants [43,44], the replacement of hydrogen in any position of the benzene ring hy a halogen atom leads to an increase in the strength of the substituted acid, but not in the same order as would be expected on the basis of the relative electronegativities of the halogen atoms. To explain the experimental facts required not only that the halogens have the ability to show a mesomeric effect but also their arrangement according to decreasing mesomeric effect in the same order (F > Cl > Br > I) as would give a fluorine atom attached to an aromatic system the least electronegativity and an iodine atom the greatest.

If the concepts of the quantitative theory of the reactivity of organic compounds are followed and the σ-constant of a substituent is regarded as the sum of inductive and mesomeric constituents ($\sigma = \sigma_I + \sigma_R$), the mesomeric influence of halogen atoms on the strength of, for example, *p*-halogenobenzoic acids is very pronounced. Thus in *p*-fluorobenzoic acid the aliphatic constant of the substituent (σ_I), which is 0.52, is reduced to 0.48, and in *p*-chloro-, *p*-bromo-, and *p*-iodo-benzoic acids the aliphatic constants of the substituents (0.47, 0.45, and 0.38) are reduced to 0.24, 0.22, and 0.10 respectively. Hence the mesomeric effect, if it appears in the aromatic system, reduces the aliphatic constant of the substituent by 30–90%.

Table 4. Chemical shifts of ^{13}C in monosubstituted benzenes (in magnetic units in relation to benzene).

Substituent	C–X	*ortho-*	*meta-*	*para-*
F	—35.1	14.3	—0.9	4.4
Cl	—6.4	—0.16	—1.0	2.0
Br	5.4	—3.3	—2.2	1.0
I	32.3	—9.9	—2.6	0.4
CH_3	—9.1	—0.3	—0.3	2.8
OCH_3	—30.2	14.7	—0.9	8.1
NH_2	—19.2	12.4	—1.3	9.5
$N(CH_3)_2$	—22.4	15.7	—0.8	11.5
CHO	—9.0	—1.2	—1.2	—6.0
NO_2	—19.6	5.3	—0.8	—6.0
$COCH_3$	—9.3	—0.2	—0.2	—4.2

Let us examine to what extent the information about the distribution of electronic density in substituted benzenes based on the chemical properties reflects the electronic structure of the molecules in their ground state, by comparing the chemical results with those on the magnetic resonance of ^{13}C, ^{1}H, and ^{19}F nuclei, and also let us attempt to discover certain features of the effect of the substituent (halogens and alkyl groups) on their introduction into unsaturated and aromatic systems.

As Table 4 shows, the ^{13}C chemical shifts in the meta-position in all the monosubstituted benzenes investigated are found at weaker fields relative to benzene, and with the halogens the screening decreases steadily from fluorine to iodine [45].

The chemical shifts of ^{13}C in the para-position for all the substituents without multiple bonds, including halogens and CH_3, are located at higher fields. Among the halogens the strongest screening effect is exerted by fluorine, the least by iodine. The methyl group has less influence than fluorine on the chemical shift, but more than chlorine, bromine, and iodine. In the theory of electronic displacements it is assumed that the inductive effect of the substituents is transmitted along the aromatic system of bonds to the same extent in both the meta- and the para-positions but the mesomeric effect of the substituent appears only in the ortho- and para-positions. If the relative electron densities at the carbon atoms in the meta-position were determined solely by the inductive effect then their screening under the influence of the halogens should be reduced from iodine to fluorine and not in the opposite direction, as is actually observed; under the influence of the methyl group (which is regarded theoretically as electron-repulsive) the electron density at the meta-carbon atom should be increased: in reality it is decreased in comparison with benzene. The same contradiction arose in the theory of the reactivity of organic compounds when explaining the relative strength of the *m*-halogeno-substituted benzoic acids with the aid of the inductive effect. Since, according to the theory of mesomerism the mesomeric effect can be transmitted to the reaction centre solely from the para- and ortho-position, the strength of the *m*-halogenobenzoic acids should be determined by *I*, the inductive effect of the substituent and their acidity should increase steadily from *m*-iodobenzoic to *m*-fluorobenzoic acid as occurs in the series of halogenoacetic acids. However, *m*-fluorobenzoic acid ($\sigma_m = 0.34$) is weaker than *m*-chlorobenzoic acid ($\sigma_m = 0.37$) and the latter is weaker than *m*-bromobenzoic acid ($\sigma_m = 0.39$) (see Table 5). The same sequence in the degree of dissociation is observed in the series of *m*-halogenophenols. To explain this phenomenon it was suggested [46] that the halogens (and also other similar substituents) in the meta-position bring about a mesomeric shift of π-electrons into the other-position, from which they are transmitted to the reaction centre by an *induction mechanism* as is shown by the following resonance structure (A):

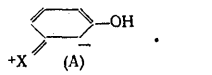


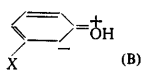
Table 5. Values of the constants δ_m, δ_m^0, δ_R^m, δ_p, δ_p^0, δ_R^0, and δ_I for the substituents.

Substituents	δ_m after Brown and Danielo	δ_p after Taft	δ_R^m	δ_p after Brown and Danielo	δ_p^0	δ_R^0	δ_I
F	0.34	0.35	—0.17	0.06	0.17	—0.35	0.52
Cl	0.37	0.37	—0.10	0.23	0.27	—0.20	0.47
Br	0.39	0.38	—0.07	0.23	0.26	—0.19	0.45
I	0.35	0.35	—0.03	0.28	0.27	—0.11	0.38
CH_3	—0.07	—0.07	—0.02	—0.17	—0.15	—0.10	—0.05
OCH_3	0.12	0.13	—0.12	—0.27	—0.12	—0.37	0.25
NH_2	—0.16	—0.14	—0.24	—0.66	—0.38	—0.48	0.10
$N(CH_3)_2$	—0.21	—0.15	—0.25	—0.83	—0.44	—0.54	0.10
CHO	0.36	—	—	0.22	—	—	—
NO_2	0.71	0.70	0.07	0.78	0.82	0.19	0.63
$COCH_3$	0.38	0.34	0.06	0.50	0.46	0.18	0.28

The displacement of π-electrons towards the reaction centre by this mechanism should proceed to such an extent that the usual series of relative electronegativity of the

halogens (F > Cl > Br > I) is reversed (F < Cl < Br < I). From the energetic point of view the assumption about the displacement of negative charge from the ortho-carbon in structure (A) to the electronegative (oxygen) and not to the electropositive centre ($X^+=$) is quite unfounded.

In connection with the problem, already discussed, of the delocalisation of π-electrons within the framework of the localised pairs method, mention must be made of the effect of resonance structure (B):



(B)

with an additional stabilising localisation of charge at the ortho-carbon.

On the basis of a procedure of partitioning the substituent constants into inductive and mesomeric constituents, Taft and Lewis quantitatively estimated the capability of meta-substituents to show a mesomeric effect (σ_R^m), by assuming that it is one-third [47] or one-half [48] the mesomeric effect of the substituents in the para-position (σ_R^0). Actually, however, the ratio σ_R^m/σ_R^0 is not constant and varies (Table 5) from 0.2 (for CH_3) to 0.5 (F, Cl, and other substituents). It is still not clear why even in a series of monotypical substituents (halogens) the transmission of the m-effect from the meta-position takes place with different intensity (for example, for Cl $\sigma_R^m/\sigma_R^0 = 0.5$ and for iodine $\sigma_R^m/\sigma_R^0 = 0.3$).

Since in a correlation analysis it is assumed that the σ-constants of the substituents are proportional to the charges induced by the substituents in the meta- or para-positions of the benzene ring, correlation between the σ-constants and ^{13}C chemical shifts should be expected. A comparison of the m-^{13}C chemical shifts with the σ_m^0-constants (Fig. 1) shows, however, the absence of a linear relation between these two parameters; for CH_3, NH_2, and $N(CH_3)_2$ there is not a correspondence, even in sign.

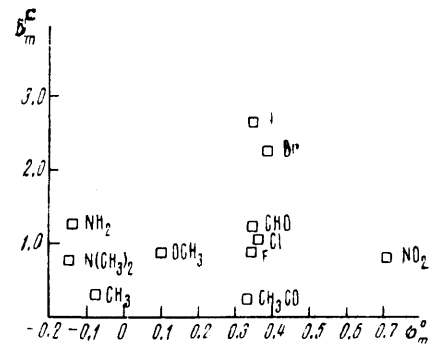


Figure 1. Comparison of the chemical shifts of m-^{13}C and the constant σ_m^0.

Judging from the values of the σ-constants of the substituents the electronic charge on the meta-carbon atoms in fluorobenzene and iodobenzene should be the same, whereas according to the NMR spectra the meta-carbon atom in iodobenzene is much less screened than that in fluorobenzene; m-chlorobenzoic acid is stronger than m-iodobenzoic acid, furthermore according to the results on the ^{13}C chemical shift m-chlorobenzoic acid should be weaker than m-iodobenzoic.

Bystrov [43] (see Chapter 1, section 7) attempted to find a correlation between the m-^{13}C chemical shifts and the inductive (δ_I) and mesomeric constants of the substituents (σ_R^m), and proposed the following equation:

$$\delta_m^C = -1.7\sigma_I + 0.82\sigma_R^m - 0.4. \quad (20)$$

Eqn. (20) is not used for halogen atoms. Actually, the experimental results show a monotonic decrease in the screening of m-^{13}C on going from fluorobenzene to iodobenzene, and according to Eqn. (20) the screening decreases in the reverse direction, from iodobenzene to fluorobenzene (the values calculated for F, Cl, Br, and I were respectively 1.57, 1.36, 1.32, and 1.14).

Table 6. ^{19}F chemical shifts in monosubstituted benzenes (in magnetic units in relation to fluorobenzene).

Substituent	*meta*-	*para*-	Substituent	*meta*-	*para*-
F	—3.03	6.80	NH_2	0.50	14.40
Cl	—2.00	3.20	$N(CH_3)_2$	—0.08	15.90
Br	—2.30	2.60	CHO	—1.30	—9.15
I	—2.40	1.70	NO_2	—3.43	—9.20
CH_3	1.23	5.40	$COCH_3$	—0.60	—6.10
OCH_3	—0.98	11.70			

We will compare the chemical shifts of m-^{13}C in halogenobenzenes with the chemical shifts of ^{19}F in m-halogenofluorobenzenes and consider the correlation between the ^{19}F chemical shifts in the latter compounds with the σ-constants of the halogens. As Table 6 shows, the ^{19}F chemical shifts in *meta*-fluoro-substituted halogenobenzenes are located in a weak field in relation to fluorobenzene and the least screening to the ^{19}F nucleus is in *meta*-difluorobenzene and then in order of screening follow I, Br, and Cl. Since the m-^{13}C chemical shifts in the halogenobenzenes alter monotonically from F to Cl the correlation between the screening of the ^{13}C nucleus and the ^{19}F chemical shifts is not expected.

Gutowsky and coworkers [49] attempted to find the relation between the ^{19}F chemical shifts in *meta*-substituted fluorobenzenes and the Hammett σm-constants. The correlation they proposed is:

$$\delta_m^F = -5.92\sigma_m \quad (21)$$

which, in general, is badly observed—for example, for ethyl m-fluorobenzoate the experimental value of σ_m^F is 2.19 m.u. (magnetic units), and the calculated value is 0.15 m.u.—particularly for the halogeno-substituted compounds. Thus the ^{19}F chemical shifts in m-difluorobenzene and m-fluoroiodobenzene are at lower fields than those in the chloro- and bromo-substituted compounds, yet according to Eqn. (21) they should be found at strong fields.

Taft [47] examined the linear relation between the ^{19}F chemical shifts in meta-substituted fluorobenzenes and the inductive constants (σ_I), expressing it by the equation:

$$\delta_m^F = -7.1\sigma_I + 0.6. \quad (22)$$

However, correlation (22) cannot be regarded as satisfactory. For various substituents there are considerable departures of the calculated values of the ^{19}F chemical shift from the experimental ones, for example, for the $CO_2C_2H_5$ group the calculated δ_m^F is −1.53 m.u. and the experimental is −0.15 m.u., for NH_2 and C_6H_5 the calculated values of δ_m^F (−0.10 and −0.10) differ from the experimental ones (respectively 0.50 m.u. and 0.15 m.u.) even in sign. The absence of a linear relation between δ_m^F and σ_I for halogens is shown in Fig. 2.

However, the problems of the accuracy with which Eqns. (21) and (22) are obeyed does not exist in considering the problem of the effect of the substituent on the electronic density at the meta-carbon atom in the compounds used for measuring the constants of the substituents, since, as Fig. 3 shows, there is no correlation between the ^{13}C and ^{19}F chemical shifts. The absence of a correlation between the m-^{13}C chemical shifts in the monosubstituted benzenes and the ^{19}F chemical shifts in the meta-substituted fluorobenzenes is not unexpected. When such a strongly electronegative atom as fluorine is introduced into the meta-position a considerable non-additive redistribution of the electron densities can take place.

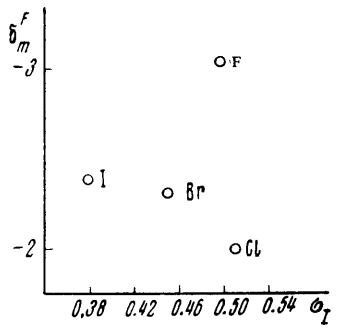


Figure 2. Comparison of the ^{19}F chemical shifts in m-halogeno-substituted fluorobenzenes with the σ_I constants.

In examining the effect of substituents on the screening of a para-carbon atom in monosubstituted benzene we must return to Table 4, from which clearly all the halogens—and also the CH_3, OCH_3, NH_2, and $N(CH_3)_2$ groups—increases the electron density at the para-carbon, and the effect decreases in the order F > Cl > Br > I.

A comparison of the p-^{13}C chemical shifts in the monosubstituted benzenes with ^{19}F chemical shifts in the para-substituted fluorobenzenes enables a correlation to be found between these two parameters, expressed by Eqn. (23):

$$\delta_p^C = 1.52\delta_p^C, \quad \delta_p^C = 0.66\delta_p^F. \tag{23}$$

Although Eqn. (23) is obeyed for certain substituents (Br, I, CH_3) with moderate accuracy, it allows the degree of screening of p-^{13}C to be evaluated for those monosubstituted benzenes for which there are no experimental results on p-^{13}C chemical shifts.

There is also a correlation between the proton chemical shifts [45,51] and the ^{13}C chemical shifts [45] that can be expressed by Eqn. (24), which is satisfied for most groups:

$$\delta_p^C = 17.3\,\delta_p^H + 0.5, \tag{24}$$

where δ_p^H is the chemical shift of para-protons in m.u.

The question naturally arises as to the correspondence between the p-^{13}C chemical shifts in the monosubstituted benzenes or the ^{19}F chemical shifts in para-substituted fluorobenzenes (since there is a correlation between these two parameters) and the σ-constants of the substituents.

Gutowsky and coworkers [49] proposed the correlation equation:

$$\delta_p^F = -17.9\sigma_p + 4.84, \tag{25}$$

which expresses the relation between the ^{19}F chemical shifts and the σ_p Hammett constants, which for most substituents is not obeyed. Taft and coworkers, having proposed various versions [51-53] of equations relating the ^{19}F with the constants of the substituents, finally settled on Eqn. (26):[54]

$$\delta_p^F = -29.5\,\sigma_R^0 - 7.1\,\sigma_I + 0.6 \tag{26}$$

in which σ_I is an inductive constant, σ_R^0 a mesomeric constituent of the σ^0 constant of the substituent.

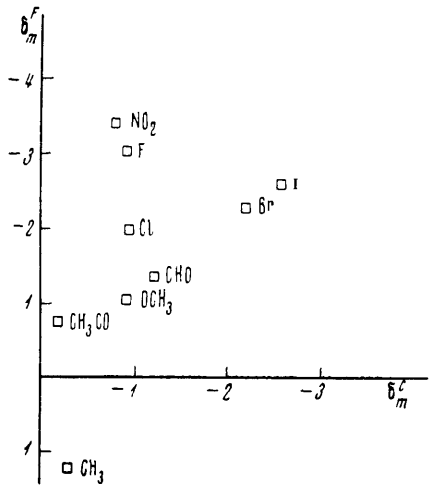
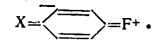


Figure 3. Comparison of the chemical shifts ^{13}C and ^{19}F of *meta*-substituted fluorobenzenes.

Hence, according to Taft, the relation between the contributions of the mesomeric and inductive effects for the reactivity of para-substituted compounds is determined by the ratio σ_R^0/σ_I, since—according to Eqn. (26)—the contributions of the mesomeric and inductive effects in the electron density of the para-carbon atom in monosubstituted benzenes is determined by the ratio $4\sigma_R^0/\sigma_I$. It is quite unknown why the influence of the mesomeric effect of the substituent in para-substituted fluorobenzene is four times its influence in para-substituted phenylacetic acids (from the dissociation constants of which the values of σ^0 are derived). On the contrary, it would appear that the introduction of a fluorine atom instead of the $-CH_2COOH$ group should (since according to the mesomerism–resonance theory the fluorine atom exhibits a large +M effect) suppress the mesomeric effect of halogen atoms in the para-position:



It must be pointed out that Eqn. (26) is satisfied by only certain substituents, and for many others there are considerable discrepancies between the calculated and experimental ^{19}F chemical shifts, for example, for Br, I, CH_3, OCF_3, CF_3, SCH_3, CN, and CH=O.

As the above shows, in the mesomeric–resonance interpretation of results on the NMR-spectroscopy of halogen-containing compounds the mesomeric effect of the halogen atoms plays an even greater part than in the treatment of acid–base equilibria.

The discrepancy between the results from ^{13}C NMR spectroscopy, which shows increased electron density at the *p*-carbon atom of halogenobenzenes, with the σ_p constants of the halogens, which indicate a decreased electron density at the carbon, linked with the reaction centre, can be attributed to various causes.

One of these could be the change in the electron density distribution of the halogenobenzene as a result of the introduction of reactive groups (OH, COOH, CH_2COOH) into its para-position, so that the halogen will show less screening of the *p*-carbon atom.

Another reason for the non-correspondence between the ^{13}C (or ^{19}F) chemical shifts and the σ_p-constants of the substituents, derivable from acid–base equilibria, could be the influence of diverse solvation processes. The role of the solvent in acid–base equilibria appears clearly in the change in the σ-constants of various substituents, especially tendency towards the formation of hydrogen bonds with water or alcohols, such as OH or NH_2. The variations in the values of the σ-constants of, for example, the OH group in *m*- and *p*-hydroxybenzoic acids with the nature of the solvent is very great and there is even a reversal of sign for the σ_m constant [55]. A considerable solvent effect on the value of the σ′-constant of bromine is observed in 4-bromocyclo[2,2,2]octane-1-carboxylic acid and the σ′-constant in this series changes particularly sharply for the $N(CH_3)_3^+$ group [56].

The σ-constants of the halogens in halogenophenols and halogenbenzoic acids change considerably on going from aqueous [57] to alcoholic solutions [58]. Thus in aqueous solution *m*-chlorophenol is less dissociated than *m*-bromo- and *m*-iodo-phenols, whereas in 50% aqueous ethanol *m*-chlorophenol is the strongest acid of these three substituted phenols. *m*-Fluorobenzoic acid is weaker than the other halogenobenzoic acids in aqueous solution but in 50% aqueous ethanol it is equal in strength to *m*-iodobenzoic acid, dissociates somewhat better than *m*-chlorobenzoic acid, and much more than *m*-bromobenzoic acid.

In aqueous solution *p*-fluorobenzoic acid ($\sigma = 0.06$) is considerably weaker than the other *p*-halogenobenzoic acids ($\sigma = 0.23–0.27$), whereas in 50% ethanol it does not differ so markedly from them ($\sigma_F = 0.20$, $\sigma_{Cl,Br,I} = 0.24–0.26$).

There are many similar examples of the pronounced differentiating effect of the solvent on relative changes in the values of the σ-constants of the substituents (for example, see Bykova and Petrova [59]).

PMR spectra are very convenient for the quantitative estimation of the influence of the solvent on the change in the electronic structure of a molecule. Diehl [60], who investigated the chemical shifts of ring protons in meta- and para-disubstituted benzenes in various solvents (hexane, acetone, benzene) found the additive nature of the effect of the substituents to be expressed as follows:

$$L_{\alpha,total} = \sum L'_{\alpha} + L_{H,\alpha}, \qquad (27)$$

where $L_{\alpha,\text{total}}$ is the total effect of the solvent α, L'_{α} the effect of the solvent α on the chemical shifts of the ortho-, meta-, and para-protons, and $L_{H,\alpha}$ the effect of the solvent on the chemical shifts of the protons of unsubstituted benzene.

By using the values found experimentally for L_H for acetone (-13×10^{-2} m.u. for a 5% molar solution in acetone) $L'_{o,x}$, $L'_{m,x}$, and $L'_{p,x}$ (listed in Table 7) the chemical shifts of the protons in monosubstituted benzenes can be found and then the changes in the electronic structure of the molecules in given solvent estimated.

The following diagrams show the chemical shifts of the protons in chlorobenzene, bromobenzene, toluene, and anisole in hexane and acetone solutions [61]:

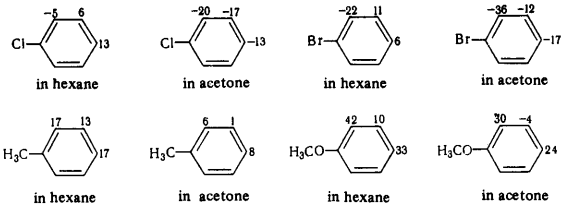


Table 7. Values of the increments L' in acetone solution (in 10^{-2} magnetic units in relation to benzene).

Substituent	L'_o	L'_m	L'_p
NH_2	−5	10	
OH	2	3	
OCH_3	1	−1	4
F	−5	−7	
CH_3	2	1	4
Cl	−2	−10	−13
Br	−1	−10	−10
I	0	−9	
CN	−9	−10	
NO_2	11	−13	

Clearly, with a polar solvent (acetone), the screening of the para-protons, and consequently also *p*-^{13}C, varies considerably. Nevertheless, as in hexane solution, the para-protons in the halogenobenzenes are screened to a greater extent than in the benzene molecule but in acetone solution they are less screened.

In acetone solution the screening of the para-protons of toluene and anisole is also reduced but nevertheless it remains greater than in benzene.

Since the polarity of water is greater than that of acetone, a change in the same order in the electron distribution in substituted benzenes also takes place in aqueous solutions. At the para-carbon atoms of the halogen-substituted compounds the charge decreases to the same extent as the electron-accepting properties of the XC_6H_4 radicals—it surpasses the electronegativity of phenyl and the *p*-halogenobenzoic acids are stronger than benzoic; the electron-accepting property of the para-tolyl and para-anisyl radicals remains less than that of the phenyl in water, as a result of which *p*-tolyl and *p*-methoxybenzoic acid are weaker than benzoic acid. Since the degree of solvation of a molecule depends both on the nature of the substituent and the type of reaction centre, the constants of the substituents do not remain constant even in a single solvent, which also explains the existence of different scales of substituents.

Let us return to a consideration of the quantum-chemical approaches to the solution of the problem of the screening of the nuclei of atoms. Karplus and Das [62] derived, on the basis of Hartree–Fock molecular wave functions, the complex relation between the ^{19}F screening in aromatic molecules and the ionic character, the order of the fluorine–carbon bond, and the hybridisation of the fluorine atom being considered. To simplify further

calculations the change in the hybridisation of the bonding orbitals of fluorine was not considered. As a result of a series of assumptions the following expression was derived for the ^{19}F chemical shifts in difluorobenzene:

$$\Delta\delta^F(\text{m.u.}) = (\delta^F - \delta^F_{\text{fluorobenzene}}) \times 10^6 = 777\,\Delta\rho - 765\,\Delta I \qquad (28)$$

where $\Delta\rho$ is the difference between the orders of the C–F π-bonds in difluorobenzene and fluorobenzene, and ΔI the difference between the polarities of the C–F sigma bond.

It was not possible to calculate the ^{19}F chemical shift in difluorobenzene from Eqn. (28) owing to the uncertainty in the values of ΔI. From the experimental results on the screening of ^{19}F in the difluorobenzenes and the calculated values of $\Delta\rho$, values of ΔI can be calculated by Eqn. (28). It appears that the contribution to the screening of ^{19}F from the mesomeric effect of fluorine is ~ 80% of the total influence of the fluorine atom found in the para-position to another fluorine atom. ΔI for *o*-difluorobenzene is negative ($\Delta I = -0.0246$), which shows that the polarity of the C–F bond is not increased when fluorine is introduced into the ortho-position of fluorobenzene; it decreases, and 75% of the total contribution to the ^{19}F screening comes from the fraction of this incomprehensively reversed inductive effect.

In the work mentioned the order of the fluorine–carbon bonds was calculated in parametric form by the molecular orbital method using the Hückel approximation (LCAO MO). It must be borne in mind that it does not follow from the approximate quantum-chemical calculations that delocalisation of the unshared pairs of electrons of the heteroatom of the substituent actually occurs; this is postulated from general considerations. The exchange interaction of an unshared pair with the π-electronic system of the aromatic ring can occur theoretically to a certain extent but it cannot exist at all if this is energetically unfavourable. In the MO method the calculation of the orders of the carbon–element bonds (the degree of double-bond character) is based on the use of parameters (estimated relative values of the coulombic and resonance integrals), arbitrarily chosen in such a way that the results of the calculations show the maximal agreement with the predictions of the resonance–mesomerism theory. The parameters for the halogen atoms are chosen in such a way that the degree of double-bond character of the carbon–halogen bond increases from iodine to fluorine, that is, so that the mesomeric effect of the halogens decreases in the order F > Cl > Br > I.

It is quite significant that in the same paper Karplus and Das compare the ^{19}F chemical shifts with the constants of the quadrupole interaction in substituted chloro- and bromo-benzenes. On the basis of the available experimental results on the asymmetry parameters for chlorobenzene ("which correspond to ~ 3% double bond nature in the C–Cl bond"), they arrived at "the important conclusion that the contribution of double-bond character to the value of $\Delta\delta$ in fluorobenzenes is significant, whereas the agreement in the values of Δq (the difference in the quadrupole interaction constants) can be reached without allowing for double-bond character in chloro- and bromo-benzenes".

In analysing the Ramsey equation for the ^{19}F screening constants with the aid of Hartree–Fock wave functions, making various assumptions about the bond parameters, Prosser and Goodman [63] derived a relation which took into account quantitatively the effect on the screening constant of the charge density of the π-electrons at the fluorine atom, the C–F bond, and the carbon atom connected with the atom being considered. The effect of the polarisation of the C–F sigma bond, that is, the influence of the inductive effect was not considered in this approximation, and the changes in the screening of the ^{19}F nuclei are explained solely by the polarisation of the π-electron cloud due to the mesomeric effect of the substituent.

According to Wu and Dailey [64] the ^{19}F chemical shift in fluorobenzene derivatives is determined by the equation:

$$\Delta\delta^F(\text{m.u.}) = \delta^F - \delta^F_{\text{fluorobenzene}} \cdot 10^6 \simeq 627\,\Delta\rho - 155.1\,\Delta P_{CF} + 574.9\,\Delta\lambda_F \qquad (29)$$

where $\Delta\rho$, ΔP_{CF}, and $\Delta\lambda_F$ denote respectively the changes in the π-electron density at the fluorine atom, the order of the C–F π-bond, and the polarity of the C–F σ-bond in the substituted fluorobenzene compared with fluorobenzene itself. The values of $\Delta\rho$ and ΔP_{CF} were calculated in that investigation by the molecular orbitals method again. The ^{19}F chemical shifts cannot be calculated by Eqn. (29), since values of $\Delta\lambda_F$ are unknown. The latter parameter was found from Eqn. (29) by use of experimental results on ^{19}F chemical shifts. As the positive values of $\Delta\lambda_F$ show, when an electron-withdrawing substituent is introduced into fluorobenzene a decrease in the polarity of the C–F σ-bond does not occur, as should happen under the inductive influence of the substituent. There is an increase in the polarity, that is, the effect of the substituent on the polarisation of the C–F bond is a mesomeric mechanism. In other words, according to Eqn. (29) the screening of ^{19}F is due solely to the mesomeric effect of the substituent (halogens, NH_2, OCH_3, CH_3).

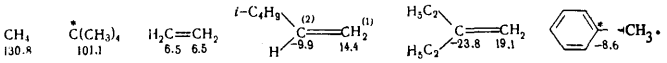
A theoretical discussion of the ^{13}C chemical shifts in substituted benzenes leads to an examination of the influence of the π-electron density and free valency at the given carbon atom, that is, with allowance solely for the mesomeric effect of the substituent [64,65].

Clearly, in the theoretical studies it is assumed that the only or the main factor which determines the screening of ^{19}F and ^{13}C in substituted benzenes is the mesomeric effect of the substituent. On the basis of what has been stated in the section on nuclear quadrupole interaction it follows that at least as regards the halogen-substituted benzenes the approach to the problem of screening in the π-electron approximation is invalid. There are evidently other factors which affect the distribution of electron density in the substituted unsaturated and aromatic systems.

We think that in examining this problem the transmission of the inductive effect of the substituent in them merits special attention. In discussing this problem the homologues of ethylene and toluene must be considered first. These are convenient models in two respects. Firstly, owing to the low polarisation of the alkyl–C bond the effect of the field in these molecules is insignificant and secondly here the influence of the mesomeric effect is excluded, since alkyl groups do not possess it [66–68].

Alkyl groups must be regarded as electron-donating substituents in comparison with hydrogen. This opinion is based on results on the relative strength of aliphatic acids, the dissociation constants of which are affected by the solvation processes. In the ground state of a molecule methyl and other alkyl groups exert an electron-withdrawing action, as should logically follow from the high electronegativity of the carbon atom compared with hydrogen and as appears from the results on magnetic resonance at ^{13}C nuclei. Thus the replacement of the hydrogen atoms in methane by methyl groups leads to a successive decrease in the screening of the central carbon [69], the introduction of alkyl radicals into the ethylene molecule causes a displacement of the signals of the ^{13}C at $C_{(2)}$ to weaker fields [70] than for ethylene, in toluene the chemical shift at $C_{(1)}$ is −8.6 m.u. in comparison with benzene. The ^{13}C

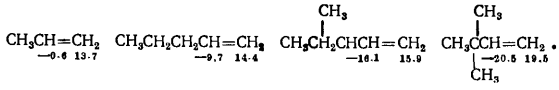
chemical shifts in relation to benzene for various compounds are as follows:



If the alkyl groups exhibited at $+I$ effect, the electronic density at $C_{(1)}$ should also be increased but to a lesser extent than at $C_{(2)}$; if the alkyl groups had a $-I$ effect (as actually happens) then the electron density at $C_{(1)}$ in the ethylene homologues would also be depressed but to a lesser extent than in $C_{(2)}$. Actually the screening of the terminal carbon $C_{(1)}$ in alkenes-1 is higher than in ethylene. Supporters of the hyperconjugation theory explain this by the mesomeric effect of the groups:

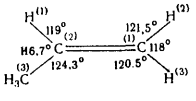
$$RCH_2CH{=}CH_2 \leftrightarrow \overset{H^+}{RCH}{=}CH{-}\overset{-}{C}H_2 .$$

Since the radicals can be arranged according to hyperconjugation effect in the order: $CH_3 > RCH_2 > R_2CH$, but the t-butyl group does not exhibit a mesomeric effect according to hyperconjugation theory, a successive decrease in the electronic charge on the terminal carbon atom of alkenes-1 would be expected on going from propene to t-butylethylene. However, in reality, as is evident from the diagrams below (the numbers denote the ^{13}C chemical shifts in relation to benzene [70]; those for propene were calculated from Savitsky and Namikava's results [71]), the order of change in the screening of the terminal carbon is the reverse of that predicted by hyperconjugation theory:



Hence the $C_{(1)}$ electron density is not determined by either the mesomeric effect of the alkyl groups (since they do not exhibit one), or the inductive effect transmitted along the carbon chain with gradual damping.

How then is the influence of the primary polarisation of the $C_{sp^3}{-}C_{sp^2}$ transmitted to the terminal carbon in alkenes-1? We think that the most important factor which determines the effect of a radical on the electron density in unsaturated and aromatic molecules is the change in its molecular structure on the introduction of a substituent, which will ensure that the potential energy of the system is a minimum. As structural investigations of propene [72] and isobutene [73] show, the replacement of hydrogen atoms in ethylene by methyl radicals involves significant changes in the geometry of the molecules. In propene $\angle H_{(1)}C_{(2)}C_{(3)} = 116.7°$, $\angle H_{(1)}C_{(2)}C_{(1)} = 119°$, and $\angle C_{(3)}C_{(2)}C_{(1)} = 124.3°$, from which it follows that the s-nature of the $C_{(2)}$ orbitals in the direction towards $C_{(1)}$ is 0.400, that is, greater than the s-nature of the orbitals of carbon in ethylene ($s = 0.368$).



From the angles of the bonds at $C_{(1)}$ it follows that the s-character of the $C_{(1)}$ orbitals in the direction towards $C_{(2)}$ ($s = 0.364$) is somewhat less than in ethylene (where $\angle HCH = 117.2°$ [74]) but the total s-character of the $C_{(1)}$ and $C_{(2)}$ orbitals ($s_{C_{(1)}} + s_{C_{(2)}} = 0.764$) exceeds the total s-character of those in ethylene ($2s_C = 0.736$), which naturally leads to an increase in the overlap of the orbitals in propene (in comparison with ethylene) and to the appearance of screening of both carbon atoms. However, the $C_{(2)}$ screening is markedly affected by the negative inductive effect of the methyl group, so that in the end $C_{(2)}$ is less screened than the carbon atoms in ethylene. The decrease in the electron density for $C_{(2)}$ is due to the displacement of the signal from $H_{(1)}$ to weaker field and correspondingly an increase in the electron density of $C_{(1)}$ brings about an increase in the screening of the $H_{(2)}$ and $H_{(3)}$ protons (in comparison with ethylene).

From the geometry of isobutene ($C_{(3)}C_{(2)}C_{(4)} = 115.3°$) there is also an increase in the overlap of the $C_{(1)}$ and $C_{(2)}$ orbitals and a greater screening of $C_{(1)}$.

In chloroethylene [28] $\angle HCCl = 113°53'$ and therefore an increase in the screening of the carbon in the CH_2 groups is to be expected. Values of 115.4° [75], 117°55', [76] and 119° [77] have been given for $\angle HCF$ in fluoroethylene. Judging by the ^1H chemical shifts in the CH_2 group of fluoroethylene, which is at a stronger field than for ethylene [78], the first value is probably the most correct.

The replacement of hydrogen in benzene by any group leads to a distortion of the regular hexagonal form of the benzene ring. This has been shown by a few but completely reliable results. Thus, in nitrobenzene [79] and benzonitrile [80] the benzene ring has the form of an irregular hexagon and in these molecules there is a change (in comparison with benzene) in both the angles and the C–C and C–H interatomic distances. Distortion of the benzene ring can have a very significant effect on the distribution of electron density and so can the change in the s-character of the carbon orbitals in the substituted benzenes which do not possess strongly polarised bonds, for example in toluene. The methyl group, which exhibits a $-I$ effect, withdraws electrons and therefore the increase in the screening of the p-carbon atom in toluene cannot be explained by the transfer of its inductive influence along the chain of atoms. Evidently the introduction of a methyl group distorts the benzene ring so that $\angle C_{(3)}C_{(4)}C_{(5)}$ becomes $> 120°$, the s-nature of the $C_{(4)}$ orbitals in the direction towards the neighbouring carbons is increased and the overlap of the $C_{(4)}$, $C_{(3)}$, and $C_{(5)}$ orbitals and the electron density at $C_{(4)}$ is increased.

If the inductive effect of the halogens (primary polarisation of the C–Hal bond), which exhibit hardly any mesomeric effects, were transferred by an aromatic system, just as in aliphatic compounds, then a decrease in the screening of the p-carbon atoms would be expected. Since the p-^{13}C-chemical shifts in the halogenobenzenes are at higher field than for benzene those changes in the hybridisation of the orbitals of carbon atoms in halogenobenzenes which facilitate the observed effect would be expected. According to one version [81] in fluorobenzene $\angle C_{(2)}C_{(1)}C_{(6)} = 121°$, $\angle C_{(1)}C_{(2)}C_{(3)} = 119°23'$, $\angle C_{(2)}C_{(3)}C_{(4)} = 119°47'$, and $\angle C_{(3)}C_{(4)}C_{(5)} = 120°40'$. In accordance with these parameters the s-character of the $C_{(4)}$ orbitals in the direction towards $C_{(3)}$ and $C_{(5)}$ is 0.338, and that of the $C_{(3)}$ and $C_{(5)}$ orbitals is 0.332. Hence in fluorobenzene the rigidity of the $C_{(4)}{-}C_{(3)}$ and $C_{(4)}{-}C_{(5)}$ bonds is somewhat above that for benzene and there is somewhat greater screening of the $C_{(4)}$ carbon atom. Naturally, during the rehybridisation of the carbon orbitals in C_6H_5X polarisation of the π-electron cloud can also take place but this is scarcely grounds for assuming considerable redistribution of it, since during the rehybridisation the electronegativity of the π-orbitals changes insignificantly (in the $trtrtr\pi$ valence state of carbon the electronegativity of the π-orbitals is 5.58 eV but in the $didi\pi\pi$ state it is 5.64 [5]).

The influence of the internal electric field of the molecules must be taken into account to a greater extent [82].

Hence we conclude that the influence of the primary polarisation of the C–X bond is transmitted in unsaturated or aromatic systems by a mechanism different from that in aliphatic or acyclic systems. Strictly speaking, the generally accepted idea that the "inductive" effect of a substituent appears in an aromatic system just as it does in an aliphatic one does not have any basis. The so-called scale of the σ_I-constants of the substituents in an aromatic system is none other than the scale of the σ_f constants of 4-substituted bicyclo[2,2,2]octane-1-carboxylic acid [83,84].

The comparison of this scale with the scale of σ_I-constants in the benzene ring [85] solely on the basis that between the bicyclo[2,2,2]octane and benzene systems there may be a geometric similarity and therefore the distribution of the $I\sigma$- and F-effects in these systems should be analogous is arbitrary. From these assumptions came attempts to separate the influence of alkyl groups and halogen atoms into inductive and mesomeric constituents, attempts which failed.

On the basis of the experimental value $\sigma'_{Br} = 0.45$ [83] and the derived value of the polar constant of the substituent for CH_2Br (1.00), Taft [85] used the relation

$$\sigma'_R = 0.45\,\sigma^*_{CH_2R} \qquad (30)$$

to calculate the $\sigma'(\sigma_I)$ constant of the substituent, since the constants $\sigma^*_{CH_2R}$ are known for a large number of substituents. However, further experimental determinations of the dissociation constants of 4-substituted bicyclo-[2,2,2]octanes carboxylic acid [84] showed that the ratio $\sigma'/\sigma^*_{CH_2R}$ is not constant for different substituents but varies from 0.08 (for CH_3) to 0.67 (for OH). From relation (30) the $\sigma'(\sigma_I)$ constants for Cl and Br are 0.45 and 0.47 respectively, whereas new experimental results have shown [84] that the σ' constant for Cl and Br are almost equal (0.471 and 0.469). It was found further that the values, calculated from (30), of the σ' constant for CH_3, OCH_3, and OH (0.045, 0.23, and 0.25 respectively) differ considerably from the experimental results—0.008, 0.30, and 0.37 respectively. On starting from the ratio $\sigma'/\sigma^*_{CH_2R} = 0.58$, which corresponds with the experimental results for the OCH_3 group, then considerable differences are found between the experimental and calculated values of σ' for various other substituents. Starting from the experimental values of $\sigma^0_p = -0.15$ and $\sigma'(\sigma_I) = -0.008$ for CH_3, it is found that $\sigma^0_R(CH_3) = -0.14$, that is, it seems that the effect of the methyl group in an aromatic system is due almost completely to its mesomeric effect (which in reality it does not exhibit at all).

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Thus the theory of mesomerism as applied to halogen-containing organic molecules does not find experimental confirmation. From an examination of the energetics of the mesomeric state of carbon–halogen bonds the arrangement of the halogens in the following order of decreasing mesomeric effect: F > Cl > Br > I (as assumed in the theory of mesomerism) is not substantiated physically. The dipole moments of halogenomethanes and halogen-substituted benzene, ethylene, and acetylene do not confirm the existence of a mesomeric effect at the halogen atoms. Variations in the lengths of the carbon–carbon bonds are explained not by the mesomeric influence of the halogens but by the hybridisation of the orbitals of the atoms which form the bond. Correlation between the lengths of the carbon–halogen bonds and the hybridisation of the orbitals of the bound atoms shows the absence of a mesomeric effect with the halogens (within the limits of accuracy of the measurements of interatomic distances).

The NQR results show that halogen atoms either do not exhibit any mesomeric effect or show it to such a small extent that it cannot have any significant influence on the physical and chemical properties of halogen-containing organic compounds.

Information about the electronic structure of organic compounds based on their reactivities does not reflect the electronic structure of the molecules in their ground state. Equilibrium constants and constants derivable from them for the substituents characterise the total influence of the substituents in non-specific and specific solvation effects on the distribution of the electronic charges in the molecule. The principal factors which determine the electron distribution on the introduction of a substituent into a molecule is the changes in hybridisation of the atomic orbitals, which ensure that the potential energy of the system is a minimum. The hybridisation of the orbitals of the σ-framework of the molecule, experimentally observable by investigations of the molecular structure of the molecules results in changes in the electronegativity of the carbon orbitals and in the polarisation of the bonds.

The inductive effect of the substituent is transmitted directly solely to the carbon atom connected with it in an unsaturated or aromatic system and subsequently its effect differs qualitatively from that in an aliphatic system.

Results on the screening of para-carbon atoms in benzene derivatives with alkyl groups or halogen atoms as substituents show that the so-called scale of inductive constants in the benzene series σ_I is a speculative concept. This scale, which is a set of constants for the substituents in the 4-substituted bicyclo[2,2,2]octane-1-carboxylic acid series does not correspond with the actual change in the electronic structure of the aromatic molecule under the influence of a non-resonating substituent. Therefore all procedures for the quantitative separation of inductive and mesomeric effects which are based on the use of a scale of inductive constants of substituents in the aromatic series are useless.

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Catalytic Dehydrogenation of Hydrocarbons

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A systematic account is given of data on certain problems in the theory of catalytic dehydrogenation relevant to the reaction mechanism and the elucidation of the nature of the active centres. The intermediate products of the hydrogenation reactions, the role of individual elementary stages, the nature of intermediate surface compounds, the side reactions of dehydrogenation catalysts, and modern hypotheses concerning the structure of the active centres are discussed. The bibliography includes 216 references.

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INTRODUCTION

Hydrocarbons of different homologous series are capable of being catalytically dehydrogenated (paraffins, naphthenes, olefins, cyclo-olefins, and alkyl-substituted aromatic hydrocarbons). The reaction results in the elimination of hydrogen and the formation of more highly unsaturated compounds or in cyclisation (dehydrocyclisation). The dehydrogenation catalysts are various metals and oxides. The principal side reactions in catalytic dehydrogenation are cracking, isomerisation, and coke formation. Catalytic dehydrogenation constitutes the basis of one of the most important types of industrial processing of hydrocarbon raw materials. Various aspects of the problem of dehydrogenation of hydrocarbons were examined in previous reviews[1-26].

II. INTERMEDIATE PRODUCTS OF DEHYDROGENATION REACTIONS

1. Olefins as Intermediates in the Aromatisation of Paraffins.

The principal products of the dehydrogenation of $C_{\geqslant 6}$ straight-chain paraffins are aromatic hydrocarbons together with a small amount of olefins. On the basis of the variation of the yield of olefins and aromatic hydrocarbons with contact time (Cr_2O_3, 475°C), Pitkethly and Steiner[27] put forward the hypothesis that heptane is aromatised via the intermediate formation of heptene.

However, a number of objections were raised against this view. Obolentsev and Usov[28] failed to observe maximum yields of olefins as a function of the time of contact under similar conditions. According to Levitskii's thermodynamic calculations[29], in the presence of large amounts of aromatic hydrocarbons the equilibrium yields of olefins are greatly reduced. On this basis, he suggested that olefins and aromatic hydrocarbons are formed simultaneously and the low yields of olefins under the conditions of high yields of aromatic hydrocarbons can be attributed to closeness to equilibrium.

Kazanskii et al.[30], who passed the Synthine fraction over platinised charcoal, failed to detect olefins although aromatisation did occur to a slight extent under these conditions.

Hypotheses concerning the mechanism of the aromatisation of paraffinic hydrocarbons omitting the olefin formation stage were developed for oxide catalysts by Plate[31], Kagan[32], and Kuo Hsie-Shien[33] and for metallic catalysts by Kazanskii, Plate, and Sergienskii[31,34,35]. In connection with this problem, we shall consider certain relations governing the formation of olefins and aromatic hydrocarbons in the catalytic dehydrogenation of paraffins. Shuikin, Timofeeva, and coworkers[36] showed that the olefin/aromatic hydrocarbon ratio greatly increases when the temperature of the dehydrogenation of hexane on an alumina–chromium oxide catalyst and the contact time are reduced. In the present author's studies[37-42], similar relations were established in the dehydrogenation of hexane on chromium oxide–magnesium oxide, chromium oxide–zinc oxide, iron oxide–alumina, and other mixed oxide catalysts and on charcoal.

A decrease in the temperature and in the contact time reduced the total amount of dehydrogenation products. This enabled the author to formulate a more general postulate[43]: a decrease of the conversion of hexane into dehydrogenation products is accompanied by an increase of the olefin/aromatic hydrocarbon ratio in the product. The above relation is valid for catalysts of various chemical compositions and prepared in different ways. Moreover, the olefin/aromatic hydrocarbon ratios and the yields of olefins and aromatic hydrocarbons fit satisfactorily on the curves describing their variation with the overall conversion in the dehydrogenation process. One of such relations is presented in Fig. 1.

Similar curves are obtained from the experimental data data of many investigators for the dehydrocyclisation of paraffins, involving straight-chain C_6-C_{10} paraffins, more than 20 catalysts, different ways of preparation of the catalysts, and different reaction conditions (temperatures in the range 450–600°C and space velocities between 0.15 and 160 h^{-1}). Fig. 2 presents the variation of the ratio of olefin yield to aromatic hydrocarbon yield with the overall yield of the dehydrogenation products.

Thus analysis of extensive experimental data shows that the main factors determining the olefin/aromatic hydrocarbon ratio is the degree of conversion of the starting material into the dehydrogenation products and changes in the chemical composition and methods of preparation of the catalyst, temperature, and the contact time are mainly important only insofar as the conversion depends on them.

The relations governing the relative yields of olefins and aromatic hydrocarbons as a function of conversion led the author to the conclusion that aromatic hydrocarbons are formed consecutively via olefins on both oxide and metallic catalysts[43,56,63-65].

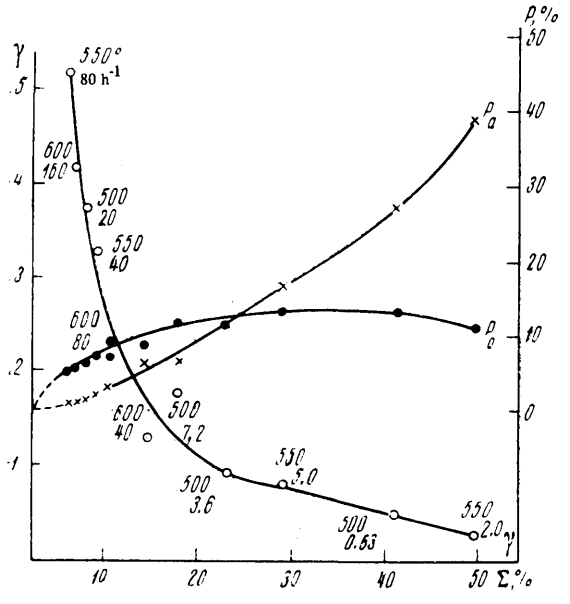


Figure 1. Variation of the yields of the heptane dehydrogenation products—olefins (P_O) and aromatic hydrocarbons (P_a)—and their ratio ($\gamma = P_O/P_a$) with the sum $\Sigma = P_O + P_a$ on the alumina–chromium oxide catalyst at 500–600°C and a space velocity of 0.63–160 h^{-1} according to the experimental data of Mattox[44].

Indeed the curves describing the yields of olefins and aromatic hydrocarbons as a function of their sum may be regarded as related to generalised kinetic curves, used for different experimental data, time having been replaced as the abscissa axis by a quantity which varies proportionately to it. The curves describing the variation of the yields of olefins and aromatic hydrocarbons (Fig. 1) exhibit the distinctive properties of consecutive reactions: the content of the intermediate (olefin) passes through a maximum with conversion and that of the final product (aromatic hydrocarbon) is initially low but increases continuously. The maxima at low yields of olefins can be accounted for by their cracking or closeness to equilibrium[65].

Similar variation of the yields of olefins and aromatic hydrocarbons with the overall degree of dehydrogenation is observed on platinum and oxide catalysts. This shows that, at least on certain metallic catalysts, olefins are also formed as intermediates in the aromatisation of paraffins.

Other data are consistent with this conclusion as well. Thus the rate of aromatisation of mono-olefins is much higher than that of paraffins (Table 1) (which may be regarded as evidence in favour of the intermediate formation of mono-olefins). Addition of hexenes to hexane increases the yields of benzene on the alumina–chromium oxide catalyst[70] and on charcoal[48].

The relative capacity of paraffins to be dehydrogenated to olefins and aromatic products did not change significantly following dilution with hydrogen[66] or on reducing the pressure in the reactor[67]; this should have been the case if the yields of olefins were limited by an equilibrium.

Table 1. Comparative data on the dehydrogenation of straight-chain paraffins and mono-olefins.

Catalyst	Temp., °C	Space velocity, h^{-1}	Yield of aromatic hydrocarbons in dehydrocyclisation, %		Refs
			heptane	heptenes	
Cr_2O_3	450		2.5	16	28
V and Al oxides	480	0.5	6	40	68
Cr, Al, and K oxides	484	0.4	37	52	32
Cr, Al, and K oxides	470	0.8	11	31	69

The conclusion that olefins are formed as intermediates in the aromatisation of paraffins on oxide and non-oxide catalysts is also confirmed by data published in recent years for experiments using tracer atoms (heptane–heptene mixtures at 487°C with contact times in the range 1.1–4 s on the alumina–chromium oxide catalyst[71] and hexane–hexene mixture at 360°C under pulsed conditions in a stream of helium on platinum and nickel[72,73].

Calculations based on Panchenkov's kinetic equation for a heterogeneous-catalytic flow reaction with consecutive stages[74] yields the ratio of the rate constants for the conversion of olefins into aromatic hydrocarbons (k_2) and of paraffins into olefins (k_1): $k_2/k_1 = 7-8$.

2. Dehydrogenation of Lower Paraffins to Mono- and Di-Olefins

In the dehydrogenation of straight-chain butane and pentanes, the products contain a certain amount of diolefins in addition to mono-olefins. The principal factors determining the mono-olefins/di-olefins ratio in the product is the degree of departure from equilibrium. The equilibrium yields of diolefins increase appreciably as the pressure is reduced and the reaction temperature increased[1,7].

Butenes are intermediates in the dehydrogenation of butane to butadiene. The work of Balandin and coworkers on the dehydrogenation of butane–butene mixtures, in which one of the components was labelled with carbon-14, led to this conclusion. The experiments were performed on chromium oxide and on the alumina–chromium oxide catalyst. A 1:1 butane–butene mixture was used in the reaction. The experiments with chromium oxide were performed at 635°C and a 1:9 dilution with water[75].

A quantitative calculation of the ratio of the rates of dehydrogenation of butane to butene (w_1) and butadiene (w_2) and of butene to butadiene (w_3) yielded the following results[76]. Under the above conditions, $w_1 : w_2 : w_3 = 20:1:1000$ for chromium oxide and $w_1 : w_2 : w_3 = 18:1:25$ for the alumina–chromium oxide catalyst (600°C, 250 mmHg), i.e. in both cases butadiene is formed from butane almost entirely via the intermediate formation of butene.

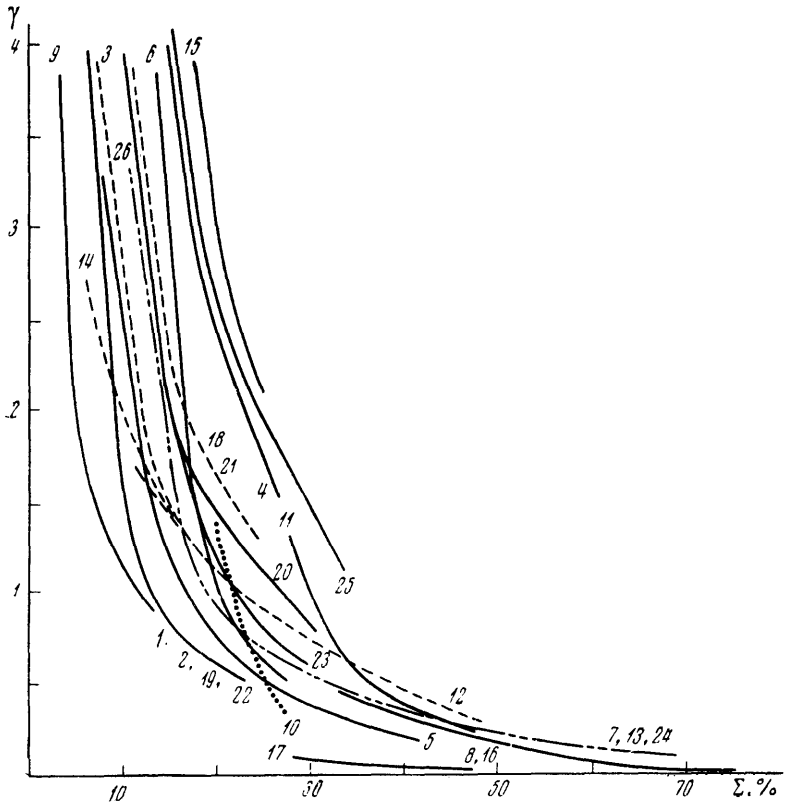


Figure 2. Comparison of the curves relating the ratios γ of olefins to aromatic products with their sum Σ: 1) hexane, Fe, Cr, and Al oxides, 500–525°C, 0.5 h^{-1} [37,39]; 2) hexane, Cr, Mg, and Zn oxides, 425–500°C, 0.5 h^{-1} [40,41]; 3) data from Fig. 1; 4) hexane, $Al_2O_3-Cr_2O_3$, 475–550°C, 0.5–2.1 h^{-1} [36]; 5) heptane, Cr_2O_3, 450–510°C [28]; 6) hexane, Cr, Al, and K oxides, 450–600°C, 9.2 h^{-1} [45]; 7) hexane, $Al_2O_3-Cr_2O_3-K_2O$, 475–527°C, 0.4–0.9 h^{-1} [46]; 8) hexane, $Al_2O_3-Cr_2O_3-K_2O$, 510–550°C, 0.37–2.5 h^{-1} [47]; 9) heptane, V and Al oxides, 450–510°C, 0.5 h^{-1} [48]; 10) heptane, Al, Cr, and Mo oxides, 490°C, 0.15–0.65 h^{-1} [29]; 11) hexane, Al and Cr oxides with Li, Na, K, Rb, Cs, Zn, or Pb additives, 500°C, 0.5 h^{-1} [49]; 12) hexane, Cr, Al, and K oxides prepared in different ways, 500°C, 0.5 h^{-1} [50]; 13) heptane, Al and Cr oxides with Be, Mg, Ca, Sr, Ba, or Zn additives, 530°C, 0.35 h^{-1} [51]; 14) heptane, Cr, K, and P oxides, 450°C, 0.8 h^{-1} [52]; 15) hexane, $Al_2O_3-Cr_2O_3$, some coke deposits, 500°C, 2.1 h^{-1} [53]; 16) heptane, K-162, some coke deposits, 515°C, 0.3 h^{-1} [54]; 17) heptane, Al, Mg, and Mo oxides, 480–530°C, 0.3 h^{-1} [55]; 18) hexane, Al, Mn, and Cr oxides, 400–550°C, 0.5–1.0 h^{-1} [56]; 19) nonane, Fe and Al oxides, 400–550°C, 0.35–1.8 h^{-1} [39]; 20) nonane and decane, Al, Cr, and K oxides, 427–600°C; 0.5–9.2 h^{-1} [45,57,58]; 21) hexane, Pt/charcoal or Al_2O_3, 300–500°C, 0.5 h^{-1} [56]; 22) hexane, MoS_2–silica gel, aluminosilicate, or MgO, 450–550°C, 0.5 h^{-1} [59]; 23) hexane, Cr_2O_3–charcoals, 370–510°C, 0.5–1.5 h^{-1} [42]; 24) hexane, $Pt-Al_2O_3-Na_2O$, 545°C, 0.4 h^{-1} [60]; 25) hexane, $Cr_2O_3-Al_2O_3$ with different porosities, 450–510°C, 0.5–2.5 h^{-1} [61]; 26) hexane, K-5, 450–530°C, 0.3–1.5 h^{-1}, dilution with hydrogen [62].

3. Dehydrogenation of Naphthenes

In the dehydrogenation of six-membered naphthenes, the main products are aromatic compounds. However, sometimes the catalytic reaction mixture contains also a small amount of unsaturated hydrocarbons.

For a long time cyclohexenes were not detected in the products of the dehydrogenation of cyclohexanes on metals. However, in a study of the initial stages of the conversion of cyclohexane on platinum, Block[77] observed by mass spectroscopy not only cyclohexene but also cyclohexadiene in the gas phase. The formation of cyclohexene and cyclohexadiene in the dehydrogenation of cyclohexane on platinum was also established by Paal and Tetenyi[78] by a pulsed technique. Here the curves relating the yields of cyclohexene and benzene to catalyst activity (which corresponds to the degree of conversion) exhibit features characteristic of consecutive reactions.

The intermediate formation of cyclo-olefins is also suggested by data from certain studies on the dehydrogenation of naphthene–cyclo-olefin mixtures by a tracer atom method. Thus cyclohexane on nickel (305–335°C) [79]

and methylcyclohexene on the alumina–chromium oxide catalyst (500°C)[80] are aromatised via an intermediate unsaturated hydrocarbon. However, direct formation of the aromatic hydrocarbon may make a considerable contribution or even predominate. Thus, in the dehydrogenation of cyclohexane on Cr_2O_3 (450°C) and holmium oxide (560°C), only about half the benzene is formed via the intermediate cyclohexene[81], and on the Pd/Al_2O_3 and Re/Al_2O_3 catalysts under reforming conditions benzene is formed almost wholly without the stage involving the intermediate cyclohexene[82].

The dehydrogenation of cyclohexane to benzene without the intermediate formation of cyclohexene can imply that either all the hydrogen atoms are eliminated simultaneously or the ease of conversion of the intermediate surface cyclohexene is much greater than the ease of its desorption. The study of the dehydrogenation of mixtures of hydrocarbons, one of which is labelled with radioactive carbon, as well as kinetic analysis cannot yield information about the stages which occur on the surface without the liberation of the reactants to the gas phase.

In the dehydrogenation of decalin and tetralin, the main product is naphthalene, but in the dehydrogenation of the first compound tetraline is also detected and in that of the second dihydronaphthalene[83]. The yield of tetralin in the dehydrogenation of decalin passes through a maximum as the temperature is increased, while the yield of naphthalene increases in the same temperature range. Dihydronaphthalene can be detected only on catalysts with low activity. Both factors – a decrease of temperature and of the activity of the catalyst—lead to decreased conversion (see Section II, 1). This suggests that the dehydrogenation of decalin proceeds via a stage involving the formation of tetralin and dihydronaphthalene. The main products of the dehydrogenation of ethylcyclohexane are ethylbenzene and styrene. Kinetic data indicate the formation of styrene via ethylbenzene[84].

Table 2. Comparison of the capacities for dehydrogenation of hydrocarbons with different degrees of unsaturation.

Hydrocarbons	Catalysts	References
Heptatriene > heptadiene > heptene > heptane	Chromium and vanadium oxides, Cr_2O_3 — Al_2O_3 — K_2O	28, 32, 68, 69, 85
Cyclohexadiene > cyclohexene > cyclohexane	Cr_2O_3, MoO_3 — Al_2O_3, Pt, Pd, Rh, Ir, Ni, Co, Fe	86–88
Cyclopentene > cyclopentane	Cr_2O_3 — Al_2O_3 — K_2O	9
Tetralin > decalin	Ni, MoO_3 — Al_2O_3	88, 89
Alkyl-substituted aromatic compounds > alkyl-substituted cycloparaffins	Mixed oxide catalyst	90
Cyclohexane > hexane	Cr_2O_3 — Al_2O_3 — K_2O	91
Hex-1-ene > cyclohexane	ditto	92

The rate of dehydrogenation of cyclic hydrocarbons as well as aliphatic hydrocarbons increases with the degree of unsaturation (Table 2), which is consistent with data on the intermediate formation of unsaturated hydrocarbons in the aromatisation of cyclohexanes.

The rate constants for the dehydrogenation of ethylcyclohexane are approximately a power of 10 lower than those for the dehydrogenation of ethylbenzene[90]. Nevertheless considerable amounts of ethylbenzene are formed in the dehydrogenation of ethylcyclohexane and can exceed greatly the yields of styrene. The low yields of styrene under the conditions of the dehydrogenation of ethylcyclohexane are evidently due to closeness to equilibrium in the dehydrogenation of ethylbenzene under the conditions of its formation from ethylcyclohexane[93].

4. Dehydrogenation of Olefins and Alkyl-Substituted Aromatic Hydrocarbons

Small amounts of more unsaturated olefins with the same number of carbon atoms are observed in the catalytic reaction mixtures when $C \geq 6$ straight-chain olefins are aromatised. Data relating the yields of dienes and aromatic hydrocarbons to the contact time and other factors which determine the conversion of mono-olefins (temperature and catalytic activity) on various catalysts (alumina–chromium oxide–potassium oxide, nickel, and platinum) exhibit features characteristic of consecutive reactions[94–96]. Thus one can suppose that the dehydrocyclisation of hexenes and heptenes proceeds via the intermediate formation of dienes.

The relations governing the yields of the products of the aromatisation of hexadienes and heptadienes on the alumina–chromium oxide–potassium oxide and platinum catalysts suggest that direct conversion of the dienes into aromatic hydrocarbons plays a considerable role together with conversion via intermediate trienes[85,97]. In the dehydrocyclisation of C_6 and C_7 trienes, intermediate cyclohexadienes are formed[85,97].

The ratios of the yields of toluene from hept-1-ene, hepta-1,3-diene, and heptatriene on the alumina–chromium oxide–potassium oxide catalyst at 450°C are 1 : 5 : 150,[85] which agrees with the above data concerning the consecutive mechanism of the dehydrocyclisation of olefins.

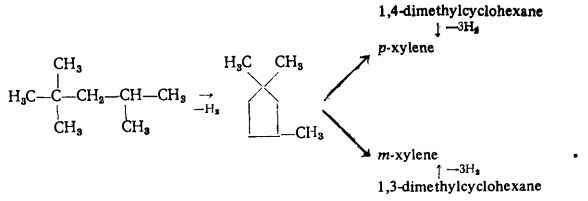
The principal products of the dehydrogenation of diethylbenzene are ethylvinylbenzene and divinylbenzene. The relations governing the yields of these products suggest that ethylvinylbenzene is an intermediate in the formation of divinylbenzene[98]. The dehydrogenation of diethylbenzene is described by the kinetic equation for a heterogeneous-catalytic flow reaction with consecutive stages[74]. On a mixed oxide catalyst at 520–560°C in a 1 : 3 diethylbenzene–water mixture, the rate constant for the dehydrogenation of ethylvinylbenzene to divinylbenzene is approximately twice as high as the rate constant for the stage involving the dehydrogenation of diethylbenzene to ethylvinylbenzene.

5. Naphthenes as Intermediates in the Aromatisation of Paraffins

In the presence of platinum on charcoal or alumina, fairly large amounts of C_5 naphthenes are formed in the paraffin dehydrogenation products. C_5-Dehydrocyclisation of paraffins to naphthenes is promoted by the presence of a five-membered carbon chain and its branching[8].

C_5-Dehydrocyclisation of paraffins is a primary reaction and does not proceed via the formation of olefins, six-membered naphthenes, or isomerisation. This is indicated by many factors[99]. Olefins are more difficult to convert into C_5 naphthenes than are paraffins; C_5-dehydrocyclisation of paraffins with six carbons atoms in the chain proceeds with greater difficulty than for carbon chains with five atoms. In all cases only those cyclopentanes are formed which should arise if the reaction

proceeded without isomerisation at all stages. Thus C_5-dehydrocyclisation of iso-octane yields 1,1,3-trimethylcyclopentane, which is partly aromatised to *m*- and *p*-xylenes under the reaction conditions:

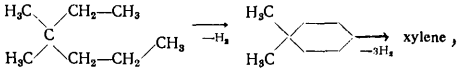


This mechanism of the aromatisation of iso-octane is supported by the following facts. The aromatisation of 1,1,3-trimethylcyclopentane on platinum/charcoal[100] and platinum–alumina[101] catalysts yields the same products (*m*- and *p*-xylenes) as in the aromatisation of iso-octane under the same conditions. On the other hand, in the presence of the alumina–chromium oxide–potassium oxide catalyst the aromatisation of iso-octane has a different mechanism: 1,1,3-trimethylcyclopentane and 2,2,4-trimethylpentane give different aromatic products[101].

In the aromatisation of straight-chain $C_{\geqslant 6}$ paraffins, C_5 naphthenes are formed to a small extent and the fraction of aromatic products formed via C_5 naphthenes becomes insignificant[102].

It has been suggested[22,31,102] that the aromatisation of unbranched $C_{\geqslant 6}$ paraffins proceeds via the intermediate formation of cyclohexanes although so far the latter could only rarely be detected in the reaction product and only in trace amounts. The difficulty of detecting cyclohexane in the dehydrocyclisation of straight-chain hexane cannot be accounted for by its high reactivity. Although cyclohexane is dehydrogenated more readily than hexane, under the usual conditions of the dehydrogenation of cyclohexane it is impossible to achieve a complete conversion [for example, cyclohexane is dehydrogenated with greater difficulty than hex-1-ene (Table 2), which is readily detected in the dehydrogenation reaction products]. In a study of the dehydrogenation of hexane–cyclohexane and hexene–cyclohexane mixtures, where one of the reactants was labelled with carbon-14, Paal and Tetenyi[78] showed recently that cyclohexane is hardly formed as an intermediate in the aromatisation of either hexane or hexene on platinum and nickel.

On the other hand, in the aromatisation of branched hexanes, the intermediate formation of six-membered naphthenes can probably make a fairly considerable contribution. Thus the formation of a conjugated bond in a paraffin containing a quaternary carbon atom is difficult: it can arise only after isomerisation or dimerisation. According to Kazanskii et al.[35], the aromatisation of 3,3-dimethylhexane on a platinum/charcoal catalyst proceeds via the intermediate 1,1-dimethylcyclohexane:



which was detected in the reaction products.

In the aromatisation of paraffins with chain lengths greater than six carbon atoms, account must be taken also of the possible formation of intermediate $C_{>6}$ naphthenes. Thus in the aromatisation of octane on a "non-acid" alumina–chromium oxide catalyst[103], methylcyclopentane, which the authors believed to be an intermediate in the formation of xylenes, was isolated.

The foregoing data show that there is an analogy in the mechanisms of the dehydrogenation of various hydrocarbons. The dehydrogenation reactions accompanied by the removal of two and more hydrogen molecules take place in steps. The intermediate product is as a rule liberated to the bulk phase before further reactions occur. In certain cases (dehydrogenation of cyclohexane to benzene), another type of reaction can predominate—direct conversion into the final product.

$C_{\geqslant 6}$ straight-chain paraffins are formed via olefins, diolefins and (to a lesser extent) triolefins. Cyclisation occurs in later stages of the reaction. This mode of reaction predominates on both oxide and metallic catalysts. The intermediate formation of five and six-membered naphthenes makes a considerable contribution to the formation of an aromatic product apparently only in the dehydrogenation of certain branched hydrocarbons.

III. MECHANISM OF CATALYTIC DEHYDROGENATION

1. Certain Elementary Steps and the Nature of Intermediate Surface Compounds

While the nature of the bulk-phase intermediate dehydrogenation products can be regarded as established in the majority of cases, there are still few data concerning intermediate surface compounds.

The dehydrogenation mechanism can be represented as a sequence of bulk-phase and surface intermediate compounds. For example, in the aromatisation of an olefin or naphthene,

$$\underset{n\geqslant 6}{C_nH_{2n}} \rightarrow \underset{0\leqslant r\leqslant 2}{(C_nH_{2n-r})} \rightarrow C_nH_{2n-2} \rightarrow \underset{0\leqslant r_1\leqslant 2}{(C_nH_{2n-2-r_1})} \rightarrow C_nH_{2n-4} \rightarrow \underset{0\leqslant r_2\leqslant 2}{(C_nH_{2n-4-r_2})} \rightarrow C_nH_{2n-6} \qquad (1)$$

(the surface compounds are indicated in brackets). Each stage of mechanism (1) can in turn consist of two or more substages and conversely not all the stages indicated are obligatory and under certain conditions there is a possibility of the simultaneous elimination of more than two hydrogen atoms from the molecule undergoing dehydrogenation or the conversion in certain stages can take place in steps but without the liberation of intermediates into the gas phase.

With increased reactivity of the hydrocarbons dehydrogenated, homogeneous stages acquire a significant importance together with surface reactions. Thus hexatrienes are known to undergo thermal cyclisation to cyclohexadiene at a temperature as low as 360°C[97,104] and at 300°C cyclohexadiene is converted into benzene[105].

According to the multiplet theory, an intermediate surface compound is formed via a two-point (doublet) or six-point (sextet) adsorption of the molecule being dehydrogenated. There must be structural and energy correspondence between the catalyst and the reacting molecule under these conditions[15].

According to Balandin, reactions such as the dehydrogenation of paraffins to olefins, of olefins to diolefins, and of alkyl-substituted to alkenyl-substituted aromatic hydrocarbons, i.e. reactions involving the dissociation of two C–H bonds, take place via a doublet mechanism. The direct dehydrogenation of cyclohexane to benzene, involving the dissociation of six C–H bonds, has a sextet mechanism. According to Liberman[99], C_5 dehydrocyclisation of paraffins to naphthenes has a sextet–doublet mechanism, in contrast to other dehydrogenation reactions:

the doublet reaction is preceded by adsorption involving a sextet mechanism.

Some data on the nature of the intermediate surface compounds of hydrocarbons were obtained recently by studying the chemisorption of hydrocarbons on catalysts by infrared and ESR spectroscopy, etc. According to modern concepts, the following types of adsorption of olefins on a metal are possible[106]:

Adsorbed at two points via σ-bonds:

$$R_aCH{=}CHR_b + 2M \rightarrow R_a\overset{M}{C}H{-}\overset{M}{C}HR_b \; ; \qquad (A)$$

associatively adsorbed via a π-electron mechanism:

$$R_aCH{=}\underset{M}{C}HR_b \; ; \qquad (B)$$

a dissociatively adsorbed olefin forming compounds of the π-allyl type:

$$R_aCH{=}CH{-}CH_2R_b + M \underset{-H}{\longrightarrow} R_aCH{-}\underset{M}{CH}{-}CHR_b \; . \qquad (C)$$

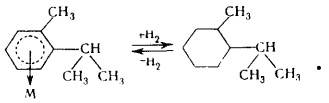
The hypothesis of the formation of an intermediate via one-point absorption does not involve a significant contribution by the geometrical factor of the kind postulated in the multiplet theory.

When an adsorbed olefin in treated with hydrogen, changes occur in the infrared spectrum, indicating the formation of surface alkyl radicals:

$$R_aCH{-}\underset{M}{CHR_b} \; (\text{or } R_aCH{=}\underset{M}{CHR_b}) \underset{-H}{\overset{+H}{\rightleftarrows}} R_aCH{-}\underset{M}{CH_2R_b} \; .$$

The adsorbed alkyl radical is evidently linked to the surface via one σ bond.

The formation of a stable partly hydrogenated form is observed also in the chemisorption of branched cyclic hydrocarbons on nickel, for example[108]:



On the other hand, under the conditions tested (room temperature, residual pressure 10^{-5} mm) the hydrogenation of adsorbed benzene yields cyclohexane, which is readily desorbed from the surface. According to the authors[107], the explanation is that an absorbed unsubstituted six-membered cyclic hydrocarbon is linked to the metal via a π bond which is weaker than a σ bond.

Under conditions approaching more closely those which actually obtain in dehydrogenation (temperatures up to 200°C), the adsorption of cyclohexane involves the formation of a surface cyclohexyl radical. This is indicated by mass-spectrometric data for the ions desorbed from platinum under the influence of a field pulse[77]. Studies of the ESR spectra also established the presence on the surface of nickel of a surface compound with a higher carbon content, which is believed[109] to be an intermediate in coke formation.

When about 10% of the nickel surface has been covered, cyclohexane has an accelerating effect on the ortho–para conversion of hydrogen, the catalytic effect increasing with the temperature of the preliminary adsorption of the hydrocarbon[110]. The acceleration of the ortho–para conversion of hydrogen is evidently related to the radical-like nature of certain surface compounds—products of the partial dissociation of the hydrocarbon molecule.

2. Cyclic Intermediates in the Aromatisation of Paraffins

Some data on the structure of the unstable intermediate compounds can be obtained by studying the dehydrogenation of hydrocarbons containing labelled carbon atoms, i.e. the variation of the product composition and of the reaction rates with the structure of the initial paraffin.

According to the Twigg–Herington hypothesis[111], the cyclisation of a linear molecule requires two-point adsorption via two carbon atoms. For example, the relative probability of the cyclisation of heptane is 4/6, since cyclisation is favoured by 1–2, 2–3, 5–6, and 6–7 adsorption but not 3–4 and 4–5 adsorption.

In a calculation of the relative probability of aromatisation, Kuo[112] began with the hypothesis of one-point adsorption. Then the probability of cyclisation should be equal to the ratio of the number of surface radicals cyclised to their total number. For heptane, the number of semihydrogenated radicals undergoing cyclisation is four, while their total number is seven and therefore the probability of cyclisation is 4/7. Kuo's mechanism, like the Twigg–Herington mechanism, allows the possibility of subsequent isomerisation of the adsorbed hydrocarbon.

According to Raik[113], the probability of cyclisation is determined by the product of the relative number of the possible collisions between the molecule and the catalyst and the relative chemical activity of the atoms. For primary, secondary, and tertiary hydrocarbons, the ratios of the first and second quantities are 3 : 2 : 1 and 1 : 2 : 10. According to this method of calculation, the relative probability of the ring-closure of heptane is 0.54.

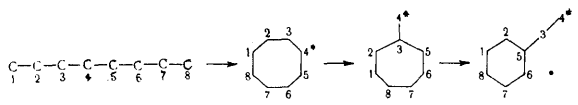
Each of the methods of calculation described explains satisfactorily in many cases the relative rates of dehydrogenation of various hydrocarbons and the composition of the aromatisation products, the differences between them involving a greater or lesser approximation to the experimental data for the individual paraffins. However, nowadays the calculation of the probability of the cyclisation of paraffins requires revision in the light of new data indicating the intermediate formation of open-chain olefins, as a result of which the cyclisation takes place at later stages than the initial adsorption of the original paraffin (see Section II, 1, 4).

The dehydrocyclisation of octane on various catalysts results in the formation of ethylbenzene and all three isomers of xylene[103,111,114–116]. According to the Twigg–Herington mechanism, ethylbenzene may be formed via 1–6 and 3–8 adsorption, and *o*-xylene via 2–7 absorption; *m*- and *p*-xylenes are formed as a result of the isomerisation of the 1–6 or 3–8 cyclic structure with intermediate formation of bicyclic species. One can also postulate isomerisation via the migration of a CH_3 group around the ring in the intermediate 2–7 surface compound[115] or as a result of an octane → iso-octane reaction[116].

However, the cyclisation of an aliphatic hydrocarbon to a six-membered ring is not the only possible pathway leading to the aromatisation of paraffinic hydrocarbons (see Section II, 5 about the formation of an intermediate five-membered ring). The numerous data of Pines and coworkers indicate other possibilities of cyclisation.

Thus one of their studies[103] dealt with the dehydrocyclisation of labelled [4-^{14}C] octane at 522°C on a "non-acid" alumina–chromium oxide catalyst, which is inactive in the isomerisation of hydrocarbons. Experiments showed that ethylbenzene is radioactive in the side chain. The displacement of the radioactive label to

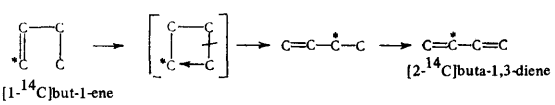
the side chain of ethylbenzene is difficult to account for otherwise than by the formation of an intermediate eight-membered ring:



The side chain contains 5–7.8% of ^{14}C, which corresponds to a 20–31% contribution of the mechanism involving the formation of a surface cyclo-octane. In order to explain the formation of other products, one must also postulate closure to a seven-membered ring and the usual six-membered ring.

Hypotheses concerning the closure of open chains to rings with various numbers of carbon atoms and the isomerisation of intermediate cyclic surface compounds have also been put forward to account for the aromatisation of hydrocarbons containing seven[117–119] and five[120,121] carbon atoms in the chain.

Cyclic intermediates and their isomerisation can play a significant role even in the dehydrogenation of lower hydrocarbons. Thus, according to recent data of Okamoto et al.[122], in the dehydrogenation of [1-^{14}C] but-1-ene over the alumina–chromium oxide catalyst there is a rearrangement involving the migration of ^{14}C from the 1-position in but-1-ene to the 2-position in buta-1,3-diene. The degree of this ^{14}C rearrangement in butadiene at 675°C is 23%. The ^{14}C rearrangement cannot be accounted for by the recombination of C_2 cracking products and indicates the formation of a four-membered ring, for example:



3. The Rate-limiting Stages and Kinetic Equations

There are data showing that the slowest stage in the dehydrogenation of various hydrocarbons is the chemical reaction. The rate of deuterium exchange involving cyclohexene and hence the rates of adsorption and desorption of cyclohexene on Pd/Al_2O_3 and Re/Al_2O_3 are much higher than the rate of dehydrogenation[123]. The same conclusion can also be reached concerning the rates of adsorption and desorption of hydrogen: the para–ortho conversion of hydrogen on Ni–ZnO is much faster than the dehydrogenation of cyclohexane[124]. Calculation of the stoichiometry for the rate-limiting stage in the dehydrogenation of butane on the alumina–chromium oxide catalyst yields a value close to unity[125].

On the assumption that the unimolecular stage of dehydrogenation on a quasihomogeneous surface is rate-limiting and that the adsorption of the reactants is described by the Langmuir isotherm, kinetic equations of the following types were derived[16] for the process under conditions far from equilibrium.

$$w = k\frac{b_i p_i}{1 + \Sigma b_i p_i}, \qquad (2)$$

where b_i are the adsorption coefficients of the reactants. Depending on the relative adsorption coefficients and the ratios of the reactant concentrations, Eqn. (2) yields effective reaction orders ranging from zero to unity with respect to the initial hydrocarbon and from –1 to 0 with respect to the product, in agreement with experiment[16,33,74,124,126–140].

This interpretation of the rate coefficients of the equations has been widely accepted. A fairly large number of determinations have been made of the adsorption coefficients of the reactants on various catalysts, including dehydrogenation catalysts. According to the available data[16,136–138,141–143], the kinetic adsorption coefficients increase in the series paraffins ≃ naphthenes ≤ aromatic hydrocarbons < olefins < diolefins and differ comparatively little on catalysts such as alumina–chromium oxide, alumina–molybdenum oxide, and nickel/Al_2O_3.

The above treatment of rate coefficients involves contradictions in a number of cases and therefore their physical significance is apparently still controversial.

Thus according to the relative adsorption coefficients, the dehydrogenation of paraffins is inhibited by the products (olefins). However, these data are inconsistent with direct measurements of the degree of adsorption. Thus the degree of chemisorption of isopentane proves to be higher than that of isopentene[144]. The hypotheses of intense adsorption of olefins are also apparently inconsistent with, for instance, kinetic dehydrocyclisation data. The consecutive equation for the dehydrocyclisation of straight-chain paraffins is valid only in the form corresponding to the intense adsorption of the product—an aromatic hydrocarbon and not an olefin[74]. At the same time, according to other data (see above), the kinetic adsorption coefficients for aromatic hydrocarbons are lower than those for olefins.

In a study published subsequently[145], it was shown by a chromatographic procedure that the degree of adsorption of hydrocarbons (paraffins and olefins) on the alumina–chromium oxide–potassium oxide catalyst under dehydrogenation conditions is lower than the degree of adsorption of hydrogen. These results make it possible to explain published data on the inhibition of the dehydrogenation of paraffins by olefins within the framework of the mechanism of the inhibition of the reaction by hydrogen[145]. One can add that sometimes in the interpretation of experimental data in terms of equations of type (2) adsorption coefficient $b_i < 0$ are obtained[146]; this is inconsistent with the assumptions made in the derivation of the kinetic equation which must be then regarded as semiempirical or it must be explained in another way. Indeed the hypothesis that the rate of the chemical reaction is limiting can hardly be regarded as universally valid, since the rates of the individual stages can vary markedly depending on the reactant and the state of the catalyst surface.

Kinetic equations analogous to Eqn. (2) or its special forms but with the constants having a different physical significance can also be derived on the hypothesis that the rate-limiting stages are the chemisorption of the initial hydrocarbon (dehydrogenation of cyclohexane on the alumina–chromium oxide catalyst)[147] or the desorption of products (dehydrogenation of methylcyclohexane on $Pt-Al_2O_3$)[148].

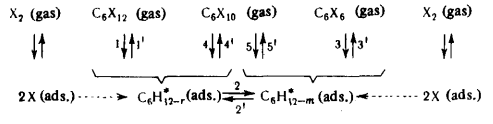
Under the usual conditions of the dehydrogenation of hydrocarbons, transfer processes apparently have a considerable influence and, at a sufficiently high temperature and for small dimensions of the catalyst pores, the rate-limiting stage may be diffusion of reactants.

The present author[61] investigated the effect of the porous structure of the alumina–chromium oxide catalyst on the conversion of hexane. Pore size was varied by

changing the intermicellar liquid. At temperatures above 470°C and for a dominant pore radius in the specimens less than 40 Å (grain size 2–5 mm), the rate of reaction was found to depend on pore size, i.e. transport processes influenced the rate of reaction. At the same time the experimental data are described fairly satisfactorily by the kinetic equation derived on the assumption that there is no diffusion-dependent inhibition.

Diffusion-dependent inhibition has also been noted by other workers: dehydrogenation of butane[7] and dehydrocyclisation of heptane[54] on alumina–chromium oxide catalysts, and dehydrogenation of cyclohexane on platinum deposited on alumina[149].

When dehydrogenation of cyclohexane and deuterium exchange involving it takes place simultaneously on the Ni–ZnO catalyst, the degree of exchange passes through a maximum with increase of temperature from 201° to 298°C, while the degree of hydrogenation increases. According to the scheme proposed by the authors[150],



(where X = H or D), the H–D exchange involving cyclohexane takes place via the intermediate surface compound $C_6H^*_{12}$ - r(ads.) and the dehydrogenation of cyclohexane involves in addition the intermediate surface compound $C_6H^*_{12}$ - m(ads.). Stages 1, 3, 4, and 5 and also the hydrogen adsorption and desorption stages are fast, while stage 2, in which one intermediate surface compound is converted into another, is slow and rate-determining.

The maximum in the rate of isotope exchange can be explained by the effect of the simultaneous occurrence of dehydrogenation on the concentration of $C_6H^*_{12}$ - r(ads.). Exchange reactions do not require the slow stages 2 or 2′ and therefore are fast even at low temperatures. With increase of temperature, the rate of dehydrogenation begins to rise sharply, which leads to a decrease of the degree of exchange. According to this mechanism, when benzene is introduced into the system, the rate of exchange falls but it does not change significantly when cyclohexene is added.

In a cordance with the data presented in Section III, 1, the compounds $C_6H^*_{12}$ - r(ads.) may be dissociatively adsorbed cyclohexene linked via two σ bonds and $C_6H^*_{12}$ - m(ads.) may be a π complex or a series of rapidly interconverted π complexes. The first surface compound may correspond to the edgewise (doublet mechanism) and the second to the planar (sextet mechanism) orientation of cyclohexane on the surface[150].

IV. VARIETIES OF THE DEHYDROGENATING EFFECT OF CATALYSTS

Dehydrogenation catalysts are extremely numerous and have a wide variety of chemical compositions. Thus, the compilation in Plate's book[31], already mentioned 51 elements as active components of catalysts for the aromatisation of paraffins and included the elements of almost all the Groups in the Periodic System, mainly Groups IV–VI. The number of known catalysts and the methods for their preparation are being continuously enlarged.

The same catalyst is capable of dehydrogenating hydrocarbons of various homologous series and structures, provided that it is sufficiently active. Thus fairly high yields of the products of the dehydrogenation of lower C_3–C_5 straight-chain paraffins, the aromatisation of C_6–C_7 straight-chain paraffins and cyclohexane, the dehydrogenation of ethylbenzene, olefins, branched paraffins, five-membered naphthenes, and alkyl-substituted hydroaromatic and other hydrocarbons have been obtained on alumina–chromium oxide–potassium oxide catalysts[9,32,70,91,151,152].

The problem of the effect of the catalyst on the relative yields of various dehydrogenation products is considered below.

1. Side and Secondary Non-dehydrogenation Reactions

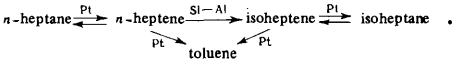
As a rule, there is no parallelism between the hydrogenating activity of catalysts and their activity in cracking and isomerisation reactions[7,31,153–155]. This suggests that the isomerisation and cracking reactions are not caused by the active centres responsible for dehydrogenation.

Numerous facts demonstrating the role of the acidity of the surface of alumina–chromium oxide catalysts in the isomerisation of paraffins have been adduced by Pines and coworkers[156].

The isomerisation of hydrocarbons on a dehydrogenation catalyst may be not only a side reaction but in certain cases may be an important stage in the dehydrogenation processes. Thus the aromatisation of paraffins with a chain length corresponding to not more than five carbon atoms must include the isomerisation stage.

When the alumina–chromium oxide catalyst is poisoned with pyridine or quinoline, there is not only a decrease in isomerising activity but also in the yields of the "abnormal" dehydrocyclisation products of octane (*m*- and *p*-xylenes), which are believed to form via a stage involving the isomerisation of octane to iso-octane or via intermediate cyclic compounds[116] (see also section III, 2).

On the other hand, under reforming conditions (hydrogen pressure, "bifunctional" catalysts), dehydrogenation may be one of the stages in the isomerisation of the hydrocarbon. Thus when heptane is brought into contact with an aluminosilicate or platinum deposited on alumina, isoheptanes are not formed. On the other hand, in the presence of these catalysts, the yield of isoheptanes is 24%. Toluene is also formed[157]. The isomerisation probably proceeds via intermediate dehydrogenation-hydrogenisation stages:



2. Dehydrogenation of Cyclohexane to Cyclohexene and Benzene

According to the multiplet theory, the dehydrogenation of cyclohexane with intermediate formation of bulk-phase cyclohexene proceeds on doublet centres, like the dehydrogenation of paraffins to olefins, and the direct dehydrogenation of cyclohexane to benzene, on sextet centres.

In early studies it was postulated that the doublet centres are characteristic of oxide catalysts and the sextet centres of metallic catalysts. Recently, with improved

experimental techniques for the investigation of catalytic reactions, an increasing number of facts have been observed, showing the intermediate formation of cyclohexene and cyclohexadiene in the presence of metallic catalysts (see Section II, 3)₣ On the other hand, Balandin and coworkers established that cyclohexane is dehydrogenated on oxide catalysts (α-Cr_2O_3), the process showing properties characteristic of sextet reactions. Therefore it is now recognised that doublet and sextet reactions can occur on both oxides and metals[15,16].

Another reason for the presence or absence of an intermediate unsaturated product in the bulk phase can probably be the capacity of the catalyst to form different types of metal–adsorbed hydrocarbon π or σ-bonds (see Section III, 1). For example the rates of desorption of cyclohexene linked to the surface by a single π bond or two σ bonds can differ markedly, as a result of which cyclohexene is evolved into the bulk phase in one case but not in the other.

3. Aromatisation and Formation of Olefins

It has been frequently postulated in the literature that the dehydrogenation of paraffins to olefins and their aromatisation on oxide catalysts take place on different active centres[31,53,158]. The fact that the olefin/aromatic hydrocarbon ratio varied within wide limits when catalysts of different chemical compositions were tested and the poisoning of an active aromatisation catalyst led mainly to decreased yields of the aromatic hydrocarbons and had much less influence on the yields of mono-olefins has been frequently put forward as the main evidence for the above hypothesis.

Thus, when the alumina–chromium oxide catalyst is poisoned with furfural or cyclopentadiene, the content of benzene in the catalytic reaction mixture in the dehydrogenation of hexane diminishes from 8–9 to less than 1% and that of alkenes from 18–19 to 6–7% (at 500°C)[53]. A similar situation was observed also in the coking of an aromatisation catalyst during the experiment[31] and when a dehydrocyclisation catalyst was poisoned with ethylene[158].

Since the dehydrogenation of higher paraffins to olefins was a more difficult problem than their aromatisation, the above concepts led to a large-scale development of studies on the choice of selective catalysts for the dehydrogenation of $C_{\geqslant 6}$ paraffins to olefins, which would be at the same time inactive in the aromatisation reaction. Various workers obtained catalysts which yielded olefins with high olefin/aromatic compound ratios or the product was altogether free of aromatic hydrocarbons[37–42,49,50,159–163]. For example, the dehydrogenation of hexane on a Cr_2O_3–AG-5 charcoal specimen at 430°C and a space velocity of 1.5 h^{-1} gave a yield of hexenes of about 10% for a selectivity of 90–95%, the yield of benzene being less than 1%.[42]

However, as pointed out for the first time by the present author[43], a high selectivity of catalysts for the formation of olefins is associated primarily with their low activity. The increase of the olefins/aromatic hydrocarbons ratio with decrease of the conversion of the starting material into dehydrogenation products is a common property of the process under consideration regardless of the causes responsible for the decrease of conversion, i.e. it is unimportant whether the decrease is a result of the deactivation of the catalysts or a change in temperature or in the contact time. Low conversions constitute a general condition for improved yields of intermediates such as olefins in the dehydrocyclisation of a paraffin.

Therefore in order to account for the experimental data on the poisoning of dehydrocyclisation catalysts as well as other data for the dependence of the relative yields of olefins and aromatic hydrocarbons on the chemical composition of catalysts, there is no need to resort to the hypothesis of the existence of two types of dehydrogenation active centres.

Previously, it was suggested[31,34] that aromatisation on oxide catalysts takes place via a doublet mechanism and on metals via a sextet mechanism. It was then believed that on oxide catalysts the dehydrocyclisation of paraffins takes place via the intermediate formation of olefins and on metals there is a direct conversion into aromatic hydrocarbons. These hypotheses were based mainly on the results of one of the early studies[30], according to which paraffinic hydrocarbons in the Synthine fraction are converted on a platinum/charcoal catalyst into aromatic hydrocarbons without the formation of olefins, the addition of which poisoned the catalyst for the aromatisation reaction.

However, subsequent studies on the aromatisation of individual hydrocarbons yielded numerous data indicating an analogy between the reactions of paraffins on oxide and non-oxide catalysts. Thus the present author's investigations[56,64,65] showed that the relative ability of platinum and also molybdenum sulphide and catalysts containing charcoals to promote dehydrogenation to olefins and aromatic hydrocarbons is almost indistinguishable from that of oxide catalysts (Fig. 2). The dehydrocyclisation of hexane on platinum and nickel as well as on oxide catalysts proceeds via the intermediate formation of olefins (Section II, 1,5). This suggests that one should not draw a distinction between metallic and oxide catalysts as regards the nature of active centres in dehydrocyclisation reactions.

The olefin/aromatic hydrocarbon ratios plotted against the sum of olefins and aromatic hydrocarbon yields on the basis of the results of different investigations give rise to a family of curves (Fig. 2) instead of a single curve as would have been expected in the ideal case if the overall conversion into dehydrogenation products constituted the only factor determining the yields of olefins and aromatic hydrocarbons. The divergence of the curves in Fig. 2 reflects the fact that the ratio of olefins and aromatic hydrocarbons in the products is influenced, apart from the overall conversion, by certain other factors. One of the principal causes of the divergence of the P_O/P_a–$(P_O + P_a)$ curves in Fig. 2 is probably the difference between the experimental methods employed in different studies or series of experiments[65]†.

In order to solve the problem of the effect of chemical composition on the relative capacity of catalysts to promote dehydrogenation to olefins and aromatic hydrocarbons (not associated with a change in activity), additional data are required which allow for other factors which may be important (for example secondary thermal reactions of the products, the presence of impurities in the raw material, etc.).

We shall consider from this point of view the results of one of the latest studies by Timofeeva[164] on the dehydrocyclisation of hexane and nonane on alumina–chromium

† This must be taken into account in the interpretation of experimental data. Otherwise, instead of the curves relating P_O, P_a, and P_p/P_a to $P_O + P_a$, more or less broad bands would have been obtained and the objection[164] against the use of the method in the study of theoretical problems would have been justified.

oxide catalysts promoted in different ways, represented by plots of the olefin/aromatic hydrocarbon ratio against the sum of olefins and aromatic hydrocarbons (Fig. 3).

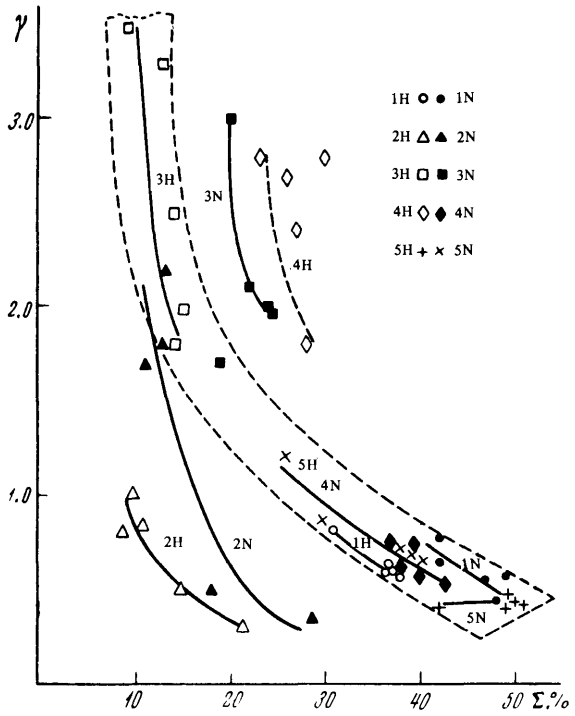


Figure 3. Plots of the ratios γ against the sum Σ of olefins and aromatic hydrocarbons based on Timofeeva's experimental data[164]; H—hexane; N—nonane: 1) $Al_2O_3-Cr_2O_3-Na_2O$; 2) K-16; 3) K-5; 4) $Al_2O_3-Cr_2O_3$; 5) $Al_2O_3-Cr_2O_3-K_2O$.

The majority of experimental points lie within a single narrow band, $P_o/P_a = f(P_o + P_a)$, in which two groups of points are distinguished: one of them refers to specimen *2* (K-16) with respect to hexane and nonane and the other to specimens *4* (alumina–chromium oxide catalyst) with respect to hexane and *3* (K-5) with respect to nonane.

Following Timofeeva[164], one could conclude on this basis that specimen *2* is somewhat less selective and specimens *3* and *4* somewhat more selective than specimens *1* and *5* (K and Na alumina–chromium oxide catalysts). However, the present author believes that such a conclusion would be premature. Indeed the results for hexane and nonane on specimens *3* and *4* do not agree. The data for hexane on specimen *4* are inconsistent with other results of the same author's[45,49,50], obtained on alumina–chromium oxide catalysts both with and without alkali metals, which fit satisfactorily on $P_o/P_a = f(P_o + P_a)$ curves (Fig. 2). The discrepancy between the olefin/-aromatic hydrocarbon ratios in Timofeeva's work[164] is probably associated with the method of analysis of the products, which was not the same in all the experiments.

The conclusion that the active centres for the dehydrogenation and aromatisation of paraffins are of the same type is consistent with the experimental data for the catalytic properties of various substances.

The most active catalysts in the dehydrogenation of lower paraffins to olefins and the aromatisation of $C_{\geq 6}$ paraffins are promoted alumina–chromium oxide catalysts and as a rule the additives introduced into the catalyst or the change in the method of preparation or the treatment of the catalyst have similar effects (activation, increase of activity with time of operation, etc.) on both reactions and also on the dehydrogenation of six-membered naphthenes (Table 3).

Table 3. Effect of certain additives on the properties of dehydrogenation catalysts.

Starting material	Additives	Hydrocarbons	Effect on catalytic properties	Refs.
$Cr_2O_3 - Al_2O_3$	Alkali metal oxides	C_3–C_7 paraffins, cyclohexane, isopentenes	Increase of activity	165–175
ditto	CaO, SrO, BaO	Butane, heptane, cyclohexane	Ditto	51, 167, 176, 177
»	Fe oxides	Butane, hexane	Decrease of activity	37, 178
»	Alkali metal oxides	Isopentane, heptane, cyclohexane	Retardation of attainment of steady activity	168, 173, 179
»	K_2O	Butane, heptane	Decrease of coke formation	167, 180
$MoO_3 - Al_2O_3$	K, Rb, Cs, Ce, Nd, and Hf oxides	Hexane, heptane cyclohexane	Increase of activity	179, 181, 182
$Pt - Al_2O_3$	Na_2O	Hexane, cyclohexane	Activity passes through a maximum	183
$Pd-Al_2O_3$ with added HF	Rare-earth oxides	Hexane, cyclohexane, methylcyclohexane	Increase of activity	185

4. Dehydrogenation of Hydrocarbons with and without a Double Bond

On the basis of the product proportions in the conversion of cyclohexane into benzene and methylcyclopentane and of methylcyclopentane into benzene and cyclohexane, Haensel et al.[186] concluded that, on treatment with sulphur-containing compounds, the activity of a fluorinated alumina–platinum catalyst for the stage involving the conversion of cyclohexene and benzene is lost but its activity in the conversion of cyclohexane into cyclohexene is not lost and therefore the above reactions take place on different active centres. The subdivision of catalyst active centres into those which dehydrogenate paraffins and olefins was adopted by Pines[156] and also certain earlier investigators.

However, when the $Pt-F-Al_2O_3$ catalyst is poisoned with thiophen, a sharper decrease of the yield of benzene is observed in the dehydrogenation of cyclohexane than in the dehydrogenation of cyclohexene[187], which is inconsistent with the data of Haensel et al.[186].

The conclusion that there is no sufficient evidence for a subdivision of active centres into those for the dehydrogenation of paraffins and olefins is arrived at by analysing the experimental data on the effect of chemical composition on the activity of the catalyst. As a rule, all active catalysts for the dehydrogenation of paraffins are also active in the dehydrogenation of olefins. That this is so is shown, for example, by data on the intermediate formation of olefins in the aromatisation of paraffins, which would not otherwise have occurred.

A parallelism is observed between the relative reactivities of saturated and unsaturated hydrocarbons on catalysts of different types on the one hand and on the relative activities of various catalysts in the dehydrogenation of these hydrocarbons on the other. Thus the reactivity of hydrocarbons increases with the degree of unsaturation on alumina–chromium oxide and alumina–molybdenum oxide catalysts, platinum, nickel, etc. (Tables 1 and 2). The differences between the specific activities of individual metals in relation to the dehydrogenation of cyclohexane, cyclohexene, and cyclohexadiene reach several powers of 10.[87] If one neglects the comparatively small changes (by a factor of 2–3), the specific activities of metals in the dehydrogenation of all three hydrocarbons can be arranged in the following sequence:

$$Pd \approx Pt \approx Rh \approx Ir > Ni > Ag \approx Cu \approx Co \approx Fe.$$

The hypothesis that the active centres for the dehydrogenation of saturated and unsaturated hydrocarbons are of the same type does not of course imply that the same catalysts should be optimal for both reactions.

The individual characteristics of the hydrocarbons can be reflected in side reactions and secondary transformations of the products. For example, the capacity of butadiene to cause the coking of the catalyst is much higher than that of butane or butene[183]. To reduce coke formation, the dehydrogenation of butene to butadiene is carried out in the presence of water vapour, which poisons alumina–chromium oxide catalysts. Therefore butenes are not dehydrogenated on the alumina–chromium oxide catalyst, but on other catalysts, which are stable in relation to water, for example the ion oxide–chromium oxide–potassium oxide catalyst.

Other factors can of course also be important, for example the ratio of the rates of the individual stages. Thus if the rate-limiting stage in the dehydrogenation of the less reactive of two hydrocarbons being compared is the chemical reaction, then the rate of dehydrogenation of the more reactive hydrocarbon on the same catalyst may be affected also by factors such as the rate of adsorption or of internal diffusion. Therefore the optimum catalysts for the two hydrocarbons should be different.

5. C_5 Dehydrocyclisation

A parallelism is not observed between the activities of various catalysts in relation to the C_5 dehydrocyclisation of paraffins and other reactions involving the dehydrogenation of hydrocarbons. Thus the activity of platinum on charcoal in the C_5 dehydrocyclisation of isooctane to 1,1,3-trimethylcyclopentane is independent of the temperature at which the catalyst is formed in the range between −10° and 40°C but, when the platinum content in the catalyst diminishes from 20 to 5%, its capacity for C_5 dehydrocyclisation falls sharply[189]. On the other hand the activity of the platinum/charcoal catalyst in the dehydrogenation of cyclohexane passes through a maximum in the first case and in the second case remains virtually unchanged.

These data, indicating that the C_5 dehydrocyclisation of paraffinic hydrocarbons to naphthenes takes place on different active centres than the dehydrogenation of cyclohexane, are consistent with the experimental data on the selection of catalysts. It is known that on many active dehydrogenation catalysts—metals (palladium, osmium, and iridium on charcoal, nickel on charcoal and alumina, etc.) and oxides—it has not so far been possible to achieve the C_5 dehydrocyclisation of paraffins, which occurs only on platinum[8,102,190]. This does not apparently apply to the C_5 dehydrocyclisation of olefins, which, in contrast to paraffins, takes place not only on platinum but also on the alumina–chromium oxide catalyst (for example, the C_5 dehydrocyclisation of dimethylpentadiene to dimethylcyclopentadiene[191].

V. MODERN HYPOTHESES CONCERNING THE NATURE OF THE ACTIVE SURFACE OF DEHYDROGENATION CATALYSTS

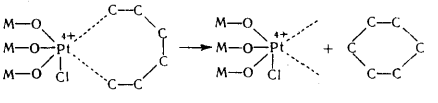
1. Platinum and Certain Metallic Catalysts

The catalytic activity of metals in dehydrogenation reactions is due to their capacity to form chemical bonds with hydrocarbon molecules in the gas phase. According to modern data[106], an olefin (A) adsorbed via two σ bonds on a transition metal is formed by the rehybridisation of the carbon atoms involved in the olefinic bond to sp^3 hybridisation with subsequent formation of two σ bonds between the carbon and metal atoms. In an olefin (B) adsorbed via a π bond, the carbon atoms are in a state of sp^2 hybridisation, the atoms and groups linked to the carbon atoms being located in almost the same plane, parallel to the surface. One surface metal atom is directly involved in the formation of the π bond. The problem of the role of surface chemical compounds formed by the catalyst metal and the carrier of the adsorbed reactant has been widely discussed in recent years. In many cases the role of active reaction centres is attributed to these compounds.

McHenry et al.[192] found in an alumina–platinum catalyst a platinum complex which may be extracted by dilute HF solution or acetylacetone. In the catalyst obtained by impregnating alumina with H_2PtCl_6 solution, the soluble platinum complex may contain also chlorine and a promoting agent—an alkali metal. Platinum may pass into an acid-soluble state not only by forming a complex with aluminium but also as a result of non-stoichiometric absorption of oxygen[193]. Therefore the soluble platinum contained in catalysts is very inhomogeneous in composition.

A partial correlation between dehydrogenating activity and the amount of soluble platinum in the catalyst has been observed in a number of studies.

Bursian et al.[194] attribute to the complex of the alumina–platinum catalyst a structure with a coordination-unsaturated Pt^{4+} ion; its participation in the dehydrocyclisation reaction takes place as shown below (for hexane):



(D)

where M is the cation of the carrier or a structural promoting agent. Thus the catalytic effect of centres containing Pt^{4+} ions is attributed to coordination properties.

A positive aspect of the hypotheses concerning the platinum complex as an active component of the catalyst is that they reflect the common features of metallic and oxide catalysts: the activity of the latter is also attributed to the presence of cations with a definite valence (see below).

However, the soluble complex present in the alumina–platinum catalyst may decompose on reduction of the catalyst to yield metallic platinum, while the activity of the catalyst is fairly high under these conditions[193]. This implies that the presence of the platinum complex is not an essential factor determining the activity of the catalyst. This is also suggested by the catalytic activity of pure metals without a carrier. A specific objection to scheme (D) is that, according to the available data, the initial intermediates in the aromatisation of hexane are hexenes and hexadienes while cyclisation takes place only subsequently and is a rapid step (Section II, 1 and 5). Therefore if the Pt^{4+} ions entering into the complex were effective only in the cyclisation stage of the aromatisation of hexane, they would behave as weak centres and would not play a significant role in catalysis.

The problem of the nature of soluble platinum is closely related to the problem of the degree of its dispersion. Thus, according to Kraft and Spindler[193], platinum dispersed to the maximum extent becomes completely solubilised by treatment with air at 500°C and after the reduction of the catalyst the degree of dispersion of platinum increases still further. The degree of dispersion of platinum and other metals on a carrier can become very high, up to atomic dispersion[195-197].

The structure of the platinum as well as the nature of the carrier were of secondary importance compared with the surface area in tests on the activity of alumina–platinum catalysts compared in different ways and containing different amounts of soluble platinum[193]. Thus the observed correlation between the content of the platinum–aluminium complex and the activity of the catalyst may be accounted for by the fact that the formation and subsequent decomposition of the complex promotes an increase in the degree of dispersion of platinum.

The affect of alkali metal promoting agents in alumina–platinum catalysts consists, apart from supressing the acid centres, in preventing the recrystallisation of platinum because the promoting agent is involved in the formation of a soluble complex.

Hypotheses have been put forward concerning the catalytic role of compounds formed by platinum and the carrier—charcoal ("pseudosandwich" complexes or a combination of platinum crystallites and graphite sextets[198-200]). However, there are still very few data on this problem.

According to Wood[201], adsorbed hydrogen is required for the dehydrogenation of cyclohexane on a metallic catalyst. This conclusion follows from the fact that, under the conditions investigated, the reaction ceased when hydrogen was completely removed from the reactor. The experiments were performed at 125°C and hydrogen was evacuated via a membrane made of the material of the catalyst (a palladium–silver alloy) which is permeable to it. Wood believes[201] that the active centre for the dehydrogenation reaction on the catalyst investigated is an adsorbed hydrogen atom.

2. Chromium Oxide and Certain Oxide Catalysts

According to modern concepts, the hydrocarbon adsorbed on a metal oxide is linked to metal ions and not to oxygen[16,202]. The formation of a bond between the adsorbed hydrocarbon and a transition metal ion takes place via unfilled *d* levels of the metal or via the formation of an *s*–*d* bond.

Some investigators[167,203] established a correlation between the amount of Cr^{6+} contained in the alumina–chromium oxide catalyst and its dehydrogenating activity and in this connection suggested that the hexavalent chromium present in the catalyst acts as a carrier of catalytic activity.

However, this hypothesis is not adequately justified, since under the reaction conditions the reduction of Cr^{6+} and other possible compounds in which the valence of chromium is greater than 3 takes place very rapidly[204], while the activity of the alumina–chromium oxide catalysts persists for a long time. In the regeneration of the alumina–chromium oxide catalyst in a stream of carbon dioxide, higher chromium oxides are not formed and yet such catalysts are not less active than those regenerated with air[205].

The amount of Cr^{6+} in the catalyst depends on the conditions and duration of oxidation and on the nature of the promoting agent. The correlation between the activity and amount of Cr^{6+} in the catalyst observed in some cases might have been due to the fact that the reduction of higher chromium oxides under the reaction conditions is nevertheless not entirely complete and the residual non-reduced chromium, being a constituent of, for example, a spinel with the aluminate of the added metal, has a promoting effect.

Van Reijen et al.[147] concluded from measurements of the magnetic moments and ESR signals of alumina–chromium oxide catalysts subjected to various types of oxidation–reduction treatment that the higher chromium oxides are reduced in a stream of dry hydrogen, i.e. under conditions favouring the formation of an active alumina–chromium oxide catalyst, not only to tervalent but also to bivalent chromium. The proportions of the bivalent and tervalent chromium oxides are determined by the equilibrium

$$2\,CrO + H_2O \rightleftarrows Cr_2O_3 + H_2\,. \qquad (3)$$

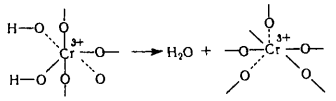
Further experimental evidence for the formation of bivalent chromium in the reduction of alumina–chromium oxide catalysts was obtained by Rubinshtein and coworkers[206]. Thus hydrogen was evolved on treatment of carefully reduced alumina–chromium oxide catalysts with water. When a catalyst reduced with deuterium was treated with water, only protium was detected in the gas. This implies that the hydrogen is formed in the decomposition of water by Cr^{2+} ions, which have reducing properties, and is not evolved as a result of desorption by water.

The amount of Cr^{2+} ions calculated from the volume of hydrogen evolved agreed approximately with the amount of hydrocarbon chemisorbed on the catalyst. On the other hand, the amount of Cr^{3+} ions present in the catalyst was approximately 40 times greater[207].

However, $CrCl_2$ is much less active in the dehydrocyclisation reaction than $CrCl_3$.[208] There are also other data which do not agree with the hypothesis that Cr^{2+} ions behave as dehydrogenation centres. Thus, according to the conditions for equilibrium in reaction (3), Cr^{2+} ions should not be present in the catalyst when the partial pressure of water vapour in the gas is greater than 1.7×10^{-3} mmHg. At the same time, at a water vapour pressure in the reacting gas of 22 mmHg, the alumina–chromium oxide catalyst retains a considerable activity[205]. On the other hand, when the partial pressure of water vapour in the gas was reduced to 3×10^{-4} mmHg, the catalytic activity fell.

The d^3 cationic structure is particularly active in reactions on semiconductors involving hydrogen[209]. The chromium ion in Cr_2O_3 has this electronic configuration. According to Kazanskii and Shvets[210], the active dehydrogenation centres are coordination-unsaturated Cr^{3+} ions.

In specimens containing adsorbed water, all the Cr^{3+} ions are in an octahedral configuration. When one water molecule is eliminated, the coordination is reduced to that of a square pyramid:



and the removal of subsequent molecules can lead to a further decrease of coordination. In order to discover if coordination-unsaturated Cr^{3+} ions present on the surface of catalysts from which water had been desorbed at high temperatures behave as dehydrogenation centres, additional studies are necessary.

Some investigators have suggested that the activity of alumina–chromium oxide catalysts is due to the formation of a specific mixed structure by the components of the catalysts. Krylova et al.[211] observed a maximum styrene content in the catalytic reaction mixture obtained in the dehydrogenation of ethylbenzene and a maximum paramagnetic susceptibility when the chromium content in the catalyst was about 2%. The maximum specific susceptibility at a low chromium content is probably associated with the formation of a Cr_2O_3 δ-phase. As regards the activity of the catalyst, one should bear in mind that chromium oxide is fairly active by itself[7,16] and the mixed alumina–chromium oxide structure would have had to be very active to play a significant role in catalysis.

However, the specimens tested[211] were relatively inactive (the styrene content in the catalytic reaction mixture was only 2–2.5 times higher than in the thermal reaction) and probably their acidity was high. Therefore the decreased yield of styrene observed when the chromium content is increased above 2% may be attributed to the formation of side products. Indeed, in the dehydrogenation of less reactive hydrocarbons (paraffins), a maximum activity was not observed in the presence of amounts of added chromium as low as 2%.[7]

Buyanov et al.[212] attribute the activity of iron oxide–chromium oxide–zinc oxide catalysts in the dehydrogenation of butenes to the presence of a chromium spinel in the catalyst composition. However, iron(III) [38,213] and zinc oxides[214] exhibit a considerable activity in the absence of chromium, let alone chromium oxide itself. Therefore the active centres in iron oxide–chromium oxide–zinc oxide catalysts can probably be the ions of any metal entering into the composition of the catalyst. On the other hand, the formation of solid solutions and mixed structures is more likely to promote the stability of the catalyst, preventing recrystallisation and undesirable chemical transformations of the catalyst, which may be particularly important in the dehydrogenation of butene and other olefins in view of the severe operating conditions of these catalysts.

The available data also do not justify the hypothesis that the dehydrogenating capacity of chromium oxide–magnesium oxide or chromium oxide–silica gel catalysts is due to the formation of mixed active structures[41,215]. The nature of the activating effect of small amounts of water remains obscure. Poorly dehydrated dehydrogenation catalysts are inactive[7]. When the water content in the starting material is increased, the activity of alumina–chromium oxide catalysts passes through a maximum.

One may suppose that water enters into the composition of the active centres of the catalyst and has a promoting effect. The reversible poisoning of the alumina–chromium oxide catalyst by larger amounts of water, can be explained by the blocking of the active centres. Indeed preliminary adsorption of water suppresses the chemisorption of hexane on the alumina–chromium oxide catalyst[216]. In this case there is only physical adsorption of hexane, which is not accompanied by dehydrocyclisation.

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The data examined show that the problem of the structure of the active centres remains controversial even for the most thoroughly investigated catalysts. In dehydrogenation reactions, metal atoms (in metallic catalysts) metal atoms or ions (in metallic adsorption catalysts), and metal ions (in oxide catalysts) can behave as carriers of catalytic activity. The composition of the active centres probably includes also chemisorbed atoms or molecules (hydrogen in the case of metallic catalysts and water in the case of the chromium oxide catalyst). The molecule undergoing dehydrogenation can be linked to the surface via one- two-, or multipoint adsorption with different types of chemical bonding (the σ bond or different varieties of coordinate bonds).

Nevertheless only a few types of dehydrogenating effect of catalysts on hydrocarbons have been observed. There is sufficient evidence to suppose that the dehydrogenation and aromatisation of paraffins takes place at the same active centres and probably this can also be said of paraffins, olefins, and naphthenes (except for the direct conversion of six-membered naphthenes into aromatic hydrocarbons).

In all these cases, where there is an analogy in the action of catalysts of different types and in the conversion of hydrocarbons of different homologous series and structures, preference should be given to the model involving an intermediate compound with one- or two-point adsorption rather than multipoint adsorption, and, among the existing hypotheses concerning the structure of the active centres, those which attribute the activity to the material of the catalyst itself and the degree of its dispersion rather than to its various compounds with carriers are to be preferred. Probably an active catalyst, such as, for example, platinum or chromium oxide, retains a considerable dehydrogenating capacity on all carriers of different types capable of ensuring that its degree of dispersion remains stable.

Conversely, the more specific dehydrogenation reactions (C_5 dehydrocyclisation of paraffins, dehydrogenation of naphthenes without an intermediate formation of cycloolefins) can be accounted for by the effect of multipoint active centres or a different type of bonding between the adsorbed molecule and the catalyst surface compared with other dehydrogenation reactions.

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Molecular Structures of Acyclic Organophosphorus Compounds

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The structural data for acyclic organophosphorus compounds published up to 1971 have been systematically reviewed. The geometrical parameters obtained for these compounds have been classified in accordance with the concepts of the valence states of the atoms in the molecules and the types of chemical bonds. Certain general relations governing the geometrical structure of the molecules have been noted on the basis of this classification. The geometrical parameters for a specific phosphorus-element bond may vary within limits greatly exceeding the experimental error as a result of the influence of the immediate environment of the bond. However, the study of the problem of the mutual influence of atoms not linked directly is difficult owing to the lack of the necessary experimental data.
The results of the determination of the conformations of acyclic organophosphorus compounds are presented.
The bibliography includes 231 references.

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I. INTRODUCTION

Since phosphorus compounds have been recently acquiring increasing practical value, it is important to investigate the characteristics of their geometrical structures, which are not only of theoretical interest but also constitute the basis for the interpretation of the rapidly increasing volume of experimental data in various branches of chemistry. The geometrical structure of molecules is characterised by certain fundamental parameters—bond length, valence angles, and angles of internal rotation. The most widely used method of calculation of bond lengths is based on systems of covalent radii[1], but it takes into account only the differences in bond multiplicity. The introduction of corrections in accordance with the Shomaker–Stevenson equation[2] makes it possible to take into account the differences between the types of atoms. However, in this case too the calculated bond lengths frequently differs from the experimental values by an amount significantly exceeding the present level of accuracy of the experimental data (about 0.01 Å).

A more logical empirical method is the phenomenological procedure, which has been particularly widely developed by Tatevskii[3-5]. The principle of the method consists in a detailed classification of bonds in molecules based on the classical theory of structure. This classification takes into account, apart from the chemical individuality of atoms and bond multiplicities, the valence state of the linked atoms (the "type" of chemical bond) and also the effect of the immediate environment. The actual role of all these factors, which influence the fundamental geometrical molecular parameters, can be discovered by analysing the experimental data. The most complete review of the stereochemistry of phosphorus compounds is given in a collective volume "Topics in Phosphorus Chemistry"[6]†.

† The Tables published under the editorship of Sutton[7] list the results of all the structural studies up to 1960 (including the studies on phosphorus compounds). There are also a number of reviews in which the stereochemistry of individual classes of organophosphorus compounds are discussed: trihalides[8], fluorides[9], sulphides[10], compounds with a P–P bond[11], compounds of pentacoordinate phosphorus[12-16], etc. Certain problems in the stereochemistry of phosphorus compounds have been examined in the monographs of Wells[17], Van Wazer[18], and Hudson[19], and in a collective volume "Topics in Stereochemistry"[20].

However, the classification of geometrical parameters in this review is not sufficiently logical and clear-cut. In addition, and this is most important, during the five years which have elapsed since the publication of this volume, new studies have expanded and deepened our knowledge about geometrical structure.

In the present review, the geometrical parameters of acyclic organophosphorus compounds have been classified on the basis of the concepts of the classical structural theory‡. Data obtained by spectroscopic (largely microwave) and diffraction (electron diffraction and X-ray diffraction) methods for the determination of molecular geometry published up to 1971 (the data published towards the end of 1970 and the beginning of 1971 are given in the Supplement) have been compiled. More accurate results have been obtained in re-investigations of the same substances. Complexes containing phosphorus–transition element bonds and salts of phosphorus acids have been excluded from consideration.

II. THE VALENCE STATES OF THE PHOSPHORUS ATOM

The phosphorus atom in various compounds coordinates between one and six ligands, but the majority of the known phosphorus compounds have coordination numbers of 3 and 4. Although phosphorus is frequently treated as an analogue of nitrogen, it is characterised by higher coordination numbers. In this respect phosphorus is closer to the heavy Group V elements—arsenic and antimony.

During recent years, compounds with dicoordinate phosphorus stable under normal conditions were obtained and investigated for the first time. In the case of acyclic structures, these are phosphamethinecyanine cations[21-23].

A large group of the phosphorus analogues of nitrogen compounds comprises derivatives of tricoordinate phosphorus. However, tervalent nitrogen can have in this case a planar bond configuration as well as a trigonal pyramidal configuration (with a minimum valence angle of

‡ The classical theory does not always give a sufficiently complete description of the chemical structure of compounds, but it does characterise satisfactorily the coordination numbers of atoms (for example, the tetracoordinate quinquevalent phosphorus in $-\overset{|}{\underset{|}{P}}=O$, $-\overset{|}{\underset{|}{P}}\rightarrow B-$, etc.).

102°). On the other hand, the average valence angles of the phosphorus atom in such compounds vary as a rule between 90° and 100°. On passing to heavier Group V elements, a tendency towards a further decrease of the average valence angle is observed§.

A tetrahedral coordination of ligands is most characteristic of the phosphorus atom. Compounds with a tetracoordinate phosphorus atom are more stable than those with different coordination. According to the classical theory of valence, there is a double bond at the phosphorus atom in such compounds (for non-ionised structures). The actual distribution of ligands can be referred to as tetrahedral in this case only in a conventional sense, since the valence angles of phosphorus within the limits of an individual structure can vary within very wide limits—from 100° to 120°. Here a double bond is involved in the formation of the largest angles.

Table 1. The limits of variation of the length of bonds between the phosphorus atom and the atoms of non-transition elements in acyclic organophosphorus compounds (in Å; on the basis of the data in Tables 2–4 and in the Addendum).

Bond	Coordination number of phosphorus					Sum of covalent radii	
	tricoordinate (single bonds)	tetracoordinate		pentacoordinate		according to Pauling (Ref.1)	with correction for heteropolarity of bond (Ref.2)
		multiple bonds	single bonds	equatorial bonds	axial bonds		
PH	1.41—1.44	—	1.39—1.41	—	—	1.40	1.40
PB	—	1.83—1.95	—	—	—	1.91	1.90
PC	1.77—1.94	1.65—1.78	1.74—1.88	1.78—1.85	1.99	1.87	1.83
PN	1.63—1.75	1.56—1.64	1.59—1.71	—	—	1.83	1.75
PO	1.60	1.43—1.51	1.52—1.61	—	—	1.84	1.71
PF	1.57—1.61	—	1.49—1.58	1.53—1.55	1.58—1.64	1.82	1.65
PSi	2.25	—	—	—	—	2.27	2.24
PP	2.19—2.21	—	2.16—2.24	—	—	2.20	2.20
PS	—	1.85—1.98	2.07—2.09	—	—	2.14	2.10
PCl	2.04—2.08	—	1.94—2.03	2.02—2.05	2.13—2.15	2.09	2.01
PGe	2.31	—	—	—	—	2.32	2.29
PSe	—	2.08—2.10	2.24—2.28	—	—	2.27	2.24
PBr	2.23	—	2.06—2.14	—	—	2.24	2.18
PI	2.43—2.48	—	—	—	—	2.43	2.38

*The distinction between multiple and single bonds is in many cases purely conventional owing to the effect of the environment (if the length of the given bond is adopted as a criterion of its multiplicity).

The stereochemistry of pentacoordinate phosphorus compounds has been the subject of extensive discussion[14,15,32-39]. Of the two most probable geometrical configurations—trigonal bipyramid and tetragonal pyramid—the first is regarded as energetically more favourable, but the energy difference is in many cases small[15].

§ In a spectroscopic study of the compounds $P(SiH_3)_3$,[24] $As(SiH_3)_3$, and $Sb(SiH_3)_3$,[25] it was suggested that their molecular skeleton is planar, in contrast to the analogues in which tin replaces silicon[26] and also $P(GeH_3)_3$.[27] However, this hypothesis was disproved by electron-diffraction[28,29] and a reinterpretation of the infrared and Raman spectra[30,31].

Studies on PX_5 compounds in the gas phase confirmed that the trigonal-bipyramidal structure is energetically more favourable¶.

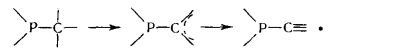
In the crystalline phase and in solution phosphorus pentahalides are present as PX_6^- anions with octahedral symmetry (tetragonal bipyramid) and tetrahedral cations PX_4^+.

As already stated, the length of a given chemical bond is determined not only by the bond type (and hence the valence state of the atoms involved in it) but also by the effect of the atoms in the immediate environment. Table 1 gives the limits of variation of the experimental phosphorus–element bond lengths in acyclic compounds for various valence states of the phosphorus atom.

III. BOND LENGTHS AND VALENCE ANGLES IN PHOSPHORUS(III) COMPOUNDS

The P—H bond length is relatively insensitive to the effect of the environment (Table 2). The difference between the values obtained by electron diffraction and spectroscopically (the microwave method) for the same molecules is systematic and is associated with the characteristics of these methods[41,42].

On the other hand, the lengths of P—C single bonds vary within wide limits, by up to 0.1 Å, which greatly exceeds the experimental error. The P—C bonds decrease in the series



As for the other element–carbon bonds, the length of each type of P–C bond varies with the type of immediate environment. Thus the length of the bond in $P(CF_3)_3$ and CF_3PH_2 molecules is much greater (by 0.05 to 0.09 Å) than in $P(CH_3)_3$. A similar relation is observed also in derivatives with nitrosyl (CF_3NO [43] and CH_3NO [44]) and carbonyl (CF_3CHO [45] and CH_3CHO [46]) groups. However, in the $N(CF_3)_3$ molecule[47] the length of the N–C bond is smaller by 0.02 Å than in $N(CH_3)_3$ and $(CH_3)_2NH$,[48] while in C_2F_6 [49] the C–C bond is shorter by 0.05 Å than in ethane[50].

The attempt to correlate the change in P–C bond lengths with a change in the C–P–C valence angle involves difficulties. The increase of this angle on passing from methyl to phenyl derivatives is replaced by a decrease in the presence of bonds. A characteristic feature of the P–N bond is that it is always shorter than the sum of the covalent radii (1.83 Å). In the amino-derivatives $X_2PN(CH_3)_2$, the configuration of the valence angles of the nitrogen atom is planar or nearly planar (the average valence angle of the nitrogen atom is $\bar{\alpha}_N = 117.5-120°$). In the ethyleneimine derivative $P[N(CH_2)_2]_3$, where the nitrogen atom forms part of a three-membered ring, $\bar{\alpha}_N$ is reduced to 101° and at the same time the shortening of the P–N bond is much less. A similar behaviour was noted also in a comparison of the structures of organic acid amides and *N*-acetylethyleneimine[51].

¶ It has been asserted in a spectroscopic study[40] that in the solid phase and in solution the $P(C_6H_5)_5$ molecule has the configuration of a square pyramid, which was subsequently disproved by an X-ray diffraction study of the crystalline substance (see Section IV, § 2).

Table 2. Geometrical parameters of acyclic organophosphorus compounds with tervalent phosphorus.

Formula	Bond type	r (PX), Å	XPY angle, deg	Method of investigation	References
		I. PH bond			
PH_3	>P—H	1.415 (0.005)	—	e.d./m.w.	52
PH_3	ditto	1.437 (0.004)	—	e.d.	53
PH_3	»	1.421 (0.005)	HPH 93.5	m.w.	54
CH_3PH_2	»	1.414 (0.003)	HPH 93.4	»	55
CH_3PH_2	»	1.423 (0.007)	—	e.d.	56
CF_3PH_2	»	1.43 (0.08)	HPH 96.7 (1.8)	m.w.	57
$C_3H_5PH_2$	»	1.413 (0.0002)		»	58
$(CH_3)_2PH$	»	1.419 (0.005)	HPC 97.0 (0.35)	»	59
$(CH_3)_2PH$	»	1.445 (0.02)	HPC 96.5 (assumed)	e.d.	56
F_2PH	»	1.412 (0.006)	HPF 96.3 (0.5)	m.w.	60
		II. PC bond			
HCP	P≡C—	1.5421 (0.0005)	—	m.w.	61
$P(CH_3)_3$	>P—C<	1.841 (0.003)	CPC 99.1 (0.2)	»	62
$P(CH_3)_3$	ditto	1.847 (0.003)	CPC 98.6 (0.3)	e.d.	63
$(CH_3)_2PH$	»	1.848 (0.003)	CPC 99.7 (0.3)	m.w.	59
$(CH_3)_2PH$	»	1.853 (0.003)	CPC 99.2 (0.6)	e.d.	56
CH_3PH_2	»	1.863 (0.003)	CPH 93.4	m.w.	55
CH_3PH_2	»	1.858 (0.003)	CPH 96.5 (assumed)	e.d.	56
$P(CF_3)_3$	»	1.937 (0.017)	CPC 99.6	»	64
CF_3PH_2	»	1.900 (0.006)	CPH 91.9 (1.9)	m.w.	57
$P(C_6H_5)_3$	>P—C<	1.828 (0.003)	CPC 103.0 (0.8)	X-ray	65
$P(C_6H_5)_2C_6H_4Br$	ditto	1.83	CPC 103	»	66
$(C_6H_5)_2P-C\equiv C-P(C_6H_5)_2$	»	1.832 (0.003)	CPC 102.8 (0.2)	»	67
	>P—C≡	1.765 (0.004)	CPC≡100.0 (0.2)		
$P(C\equiv C-C_6H_5)_3$	ditto	1.765 (0.01)	CPC≡100.7 (0.5)	»	68
$P(CN)_3$	»	1.78 (0.03)	CPC≡93.5 (2.0)	»	69
$P(C_3H_5)_3$	>P—C<	1.832 (0.006)	CPC 98.6 (1.3)	e.d.	70
$C_3H_5PH_2$	ditto	1.834 (0.0002)	CPH 98.3 (0.02)	m.w.	58
		III. PN bond			
$P[N(CH_3)_2]_3$	>P—N<	1.700 (0.005)	NPN 96.5 (1.0)	e.d.	71
$(CH_3)_2NPCl_2$	»	1.69 (0.03)	NPCl 100.0 (1.0)	»	72
$(CH_3)_2NPF_2$	»	1.628 (0.005)	NPF 101.6 (0.2)	X-ray	73
$P[N(CH_2)_2]_3$	>P—N<	1.75 (0.01)	NPN 97.5 (1.5)	e.d.	71
		IV. PO bond			
$P(OC_2H_5)_3$	>P—O—	1.600 (0.006)	OPO 96.5 (0.5)	e.d.	74
$P(OC_2H_5)_3$	ditto	1.600 (0.006)	OPO 100.0 (1.0)	»	74
CH_3OPCl_2	»	1.63 (assumed)	OPCl 99.0 (1.0)	»	75
		V. PF bond			
PF_3	>P—F	1.570 (0.001)	FPF 97.8 (0.2)	e.d./m.w.	76
F_2PH	ditto	1.582 (0.002)	FPF 99.0 (0.2)	m.w.	60
$(CH_3)_2NPF_2$	»	1.610 (0.004)	FPF 91.5 (0.3)	X-ray	73
$PFCl_2$	»	1.55 (0.05)	102 (mean)	e.d.	77
		VI. PSi bond			
$P(SiH_3)_3$	>P—Si—	2.248 (0.003)	SiPSi 96.45 (0.5)	e.d.	28
		VII. PP bond			
P_2I_4	>P—P<	2.212 (0.06)	PPI 94	X-ray	78
		VIII. PCl bond			
PCl_3	>P—Cl	2.043 (0.003)	ClPCl 100.1 (0.35)	m.w.	79
PCl_3	ditto	2.042 (0.002)	ClPCl 100.2 (0.15)	e.d.	80
$(CH_3)_2NPCl_2$	»	2.083 (0.005)	ClPCl 98.0 (1.0)	»	72
CH_3OPCl_2	»	2.084 (0.005)	ClPCl 99.3 (1.0)	»	75
$PFCl_2$	»	2.02 (0.03)	102 (mean)	»	77
		IX. PGe bond			
$P(GeH_3)_3$	>P—Ge—	2.308 (0.003)	GePGe 95.4 (0.05)	»	29

Table 2 continued.

Formula	Bond type	r (PX), Å	XPY angle, deg	Method of investigation	References
		X. PBr bond			
PBr_3	>P—Br	2.23 (0.01)	BrPBr 100 (2.0)	»	81
		XI. PI bond			
PI_3	>P—I	2.43 (0.04)	IPI 102 (2)	»	82
P_2I_4	ditto	2.475 (0.028)	IPI 102.3	X-ray	78

*Compounds with more than one type of bond at the phosphorus atom are quoted in several places according to the number of bond types. To avoid unnecessary repetition, in each case only those angles are quoted in the formation of which the given bond is involved. Here and henceforth the following notation is employed: e.d. = electron diffraction; m.w. = microwave spectroscopy; X-ray = X-ray diffraction.

It is interesting that, in contrast to the >P–N< and >P–N< bonds, the >P–C– and >P–C< bonds are hardly different in length. This is evidence of a difference in the type of interaction of tricoordinate phosphorus with nitrogen and carbon.

When two amino-groups in $P[N(CH_3)_2]_3$ are replaced by halogen atoms (chlorine, fluorine), there is a tendency towards a decrease of the P–N bond length, which is particularly pronounced in the case of the fluoro-derivative.

The effect of the amino-group on the phosphorus–halogen bond is in turn shown by a considerable increase in the length of the latter. Thus the P–Cl bond in $(CH_3)_2NPCl_2$ is longer by 0.04 Å compared with the value found for PCl_3 and the P–F bond in $(CH_3)_2NPF_2$ is longer by the same amount compared with the value found in PF_3.

The effect of the methoxy-group is similar. The P–Cl bond in CH_3OPCl_2 is also longer by 0.04 Å than in PCl_3.

A tendency towards a decrease of the >P– element bond length compared with the sum of the covalent radii on passing along a series of elements in the Periods from left to right and in the Groups from below upwards is noteworthy (Table 1).

IV. BOND LENGTHS AND VALENCE ANGLES IN PHOSPHORUS(V) COMPOUNDS

1. Structures with a Tetracoordinate Phosphorus Atom

The vast majority of data presented in this section were obtained by X-ray diffraction studies on crystals. The structure of the molecules in crystals may be modified under the influence of the crystal lattice forces, intermolecular hydrogen bonds, etc. Moreover, the accuracy of the X-ray method for the determination of the fundamental geometrical parameters is lower than that of the electron diffraction and microwave methods. Therefore here

a detailed determination of the geometrical structure is even more complicated than in the case analysed above.

Quinquevalent tetracoordinate phosphorus forms, in contrast to tervalent phosphorus, a multiplicity of stable compounds with double bonds (as understood in the classical theory structure) (Tables 1 and 3A). The lengths of these bonds vary within wide limits (by as much as 0.15 Å) but in general are shorter than the lengths of single bonds formed by tetracoordinate phosphorus (Tables 1 and 3B).

Recently new more reliable X-ray diffraction data on the P=C bond length in phosphoranylidines have been published. The P=C bond lengths in the $(C_6H_5)_3P{=}C{=}C{=}O$, $(C_6H_5)_3P{=}C{=}C{=}S$, and $(C_6H_5)_3P{=}CH_2$ molecules were found to be appreciably shorter than in other ylidines. In the oxygen derivative the P=C=C angle is 145.0°, which is unusual for carbon, since theoretically the cumulene chain should be linear, as in carbon dioxide[83], keten[84], etc. In the thio-derivative, the length of the P=C bond is greater by 0.04 Å and the P=C=C angle is greater by 22.5°C than in the oxygen derivative. In $(C_6H_5)_3P{=}CH_2$ the P=C bond length is intermediate in the above set of three compounds. Electron diffraction data indicate a pronounced dependence of the P=O bond length on the nature of the environment. It increases by 0.04 Å on passing from $POCl_3$ to $(CH_3)_3PO$, which is accompanied by a decrease of the O–P–X angle. A similar increase of the P=O bond length occurs when one of the chlorine atoms of $POCl_3$ is replaced by C_6H_5 or $(CH_3)_2N$ groups.

It is striking that complex formation involving POX_3 (X = Cl, CH_3, C_6H_5, etc.) molecules proceeds via the phosphoryl bond and is accompanied by an increase in its length.

The single bonds in compounds of tetracoordinate phosphorus are as a rule shorter and the valence angles between them are larger than the corresponding bonds and angles in compounds with tricoordinate phosphorus (Tables 1, 2, and 3B). This relation holds satisfactorily for P–C bonds with carbon atoms in various valence states and in the majority of other cases. At the same time the P–P bond length remains constant (albeit within the limits of a considerable experimental error) for both valence states of the phosphorus atoms and is equal to the sum of the covalent radii. Some of the features of the mutual influence of atoms found in compounds of tricoordinate phosphorus (Section III) are characteristic also of compounds with tetracoordinate phosphorus. In particular, this is confirmed by the shortening of the C–N bond under the influence of fluorine atoms in the $(CH_3)_2NPF_2.B_4H_8$ molecule by 0.06 Å compared with the length of this bond in $(NH_2)_3P.BH_3$. The P–F bond length in the first molecule then proved to be significantly greater than in the absence of the amino-group (an increase by up to 0.07 Å compared with the P–F bond length in $PF_3.B_4F_6$). The effect of the amino-group on the PCl bond length is similar.

The sensitivity of the P–Cl bond to the influence of substituents is characterised by a marked tendency towards an increase in its length on passing along the series $POCl_3 \rightarrow PSCl_3 \rightarrow C_6H_5POCl_2 \rightarrow (CH_3)_2NPOCl_2$ [in the case of tricoordinate phosphorus we have similarly $PCl_3 \rightarrow (CH_3)_2NPCl_2$, CH_3OPCl_2]. The increase of the phosphorus–halogen bond length is accompanied as a rule by a decrease of the halogen–phosphorus–halogen valence angles formed by these bonds.

Complex formation via the P=O or P=S multiple bonds evidently has little effect on the P–C bond length, while the P–Cl bond length becomes appreciably reduced under these conditions.

We also have the following interesting facts.

1. The average $=\overset{|}{\underset{|}{P}}-N\diagup\diagdown$ bond length is greater by only 0.015 Å than the $-\overset{|}{\underset{|}{P}}=N-$ bond length in the $(C_6H_5)_2P(F){=}NCH_3$ molecule (Table 3A). The P–F bond is unusually short in this molecule (1.488 Å).

2. In the compound $PS[N(CH_2)_2]_3$ the $=\overset{|}{\underset{|}{P}}-N\diagup\diagdown$ bond length proved to be the same, within the limits of experimental error, as that of the $=\overset{|}{\underset{|}{P}}-N\diagup\diagdown$ bond. In contrast, as already mentioned, in compounds of tricoordinate phosphorus the $\diagup P-N\diagup\diagdown$ bond length is greater by 0.05 Å than that of the $\diagup P-N\diagup\diagdown$ bond (Table 2). The relative magnitudes of the average valence angles at the nitrogen atoms in $-N\diagup\diagdown$ and $-N\diagup\diagdown$ are the same in both cases (100–101° and 116–120°).

3. In the compound $\begin{matrix}(NH_2)_2P(S)\\ \diagdown\\ N-CH_3\\ \diagup\\ NH_2(NHCH_3)P(S)\end{matrix}$, the lengths of the bonds between the phosphorus atoms and the central nitrogen atom (1.708 Å—the maximum value known for the P–N bond length involving tetracoordinate phosphorus†) is greater by 0.06 Å than the lengths of the remaining P–N bonds in this molecule‡. The central nitrogen atom has in this case a planar bond configuration.

For comparison, we recall that the length of the Si–N bond also increases with the number of Si atoms linked to the N atom in the sequence $ClSi[N(CH_3)_2]_3$ (1.715 Å) [85] → $CH_3N(SiH_3)_2$ (1.726 Å) [86] → $N(SiH_3)_3$ (1.738 Å).[87]

2. Structures with a Pentacoordinate Phosphorus Atom

These compounds are relatively unstable. In particular, the stability of pentahalides diminishes significantly with increasing atomic weight of the halogen. The pentaiodide is altogether unknown and the chloride and bromide are ionised in the crystal to $[PCl_4]^+[PCl_6]^-$ and $[PBr_4]^+Br^-$.

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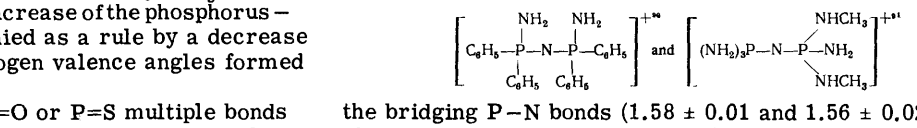
† The P–N bond length in the $Na^+[PO_3NH_3]^-$ crystal structure, which is 1.77 ± 0.02 Å, was determined by Cruickshank[88] as the length of a single P–N bond. It is close to the sum of the covalent radii of the phosphorus and nitrogen atoms with the Shomaker–Stevenson correction (1.75 Å).

In the $Ca_{1.5}C_3H_3N_2(PO_3)_2.6H_2O$ crystal structure, where the nitrogen atoms form part of an aromatic group, the average length of the P–N bonds outside the ring is 1.786 ± 0.006 Å.[89] The authors of this investigation claim that they found the length of a single P–N bond.

‡ In the cations



and

the bridging P–N bonds (1.58 ± 0.01 and 1.56 ± 0.02 Å) are shorter than the terminal bonds (1.65 ± 0.01 and 1.63 ± 0.02 Å). The P–N–P angles in these structures are 136° ± 1° and 129.2°.

Table 3. Geometrical parameters of acyclic organophosphorus compounds with tetracoordinate phosphorus.

A. Multiple bonds

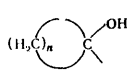
Formula	Bond type	r (P = X), r (P→X), Å	YP = X angle, deg	Method of investigation	References
1	2	3	4	5	6
I. PB bond					
$PF_3 \cdot BH_3$		1.836 (0.012)		m.w.	92
$HF_2P \cdot BH_3$	ditto	1.832 (0.009)	{FPB 117.7 (0.3) HPB 120.1 (0.6)	ditto	93
$PF_3 \cdot B_4F_6$	»	1.825 (0.015)	FPB 116.2 (1.0)	X-ray	94
$(NH_2)_3P \cdot BH_3$	»	1.887 (0.015)	NPB 115 (mean)	ditto	95
$(CH_3)_2NPF_2 \cdot B_4H_8$	»	1.856 (0.008)	{NPB 117.6 (0.3) FPB 115.0 (mean)	»	96
$(CH_3)_4P_2 \cdot 2BH_3$	»	1.951 (0.021)	{CPB 114.8 (1.4) PPB 112 (mean)	»	97
II. P=C bond					
$(C_6H_5)_3P{=}CH_2$		1.661 (0.008)	CP=C 113.5 (0.3)	»	98
$(C_6H_5)_3P{=}C{=}C{=}O$		1.648 (0.007)	CP=C 111.5 (0.4)	»	99
$(C_6H_5)_3P{=}C{=}C{=}S$	ditto	1.677 (0.008)	CP=C 110.8 (0.4)	»	100
$(C_6H_5)_3P{=}C(CH_3O_2C)-C(CO_2CH_3){=}N-C_6H_4Br$		1.70 (0.03)		»	101
$(C_6H_5)_3P{=}CH-SO_2-O-C_6H_4CH_3$	ditto	1.71 (0.02)	CP=C 107	»	102
$(C_6H_5)_3P{=}C(Cl)-C(=O)-C_6H_5$	»	1.74 (0.01)	CP=C 106	»	103
$(C_6H_5)_3P{=}R{=}P(C_6H_5)_3$ ("blue substance")	»	1.74 (mean)	approx. tetrahedral val. angles at P	»	104
$(C_6H_5)_3P{=}R$ ("dark-green substance")	»	1.77 (0.02)	CP = C 111	»	105
$(C_6H_5)_3P \cdot CS_2$	»	1.78 (0.03)	approx. tetrahedral val. angles at P	»	106
$(C_6H_5)_3P{=}C(P(C_6H_5)_3)C(CF_3)_2O$	»	1.75 (0.02)	CP = C 114.1 (mean)	»	107
III. P=N bond					
$(C_6H_5)_2P(F){=}NCH_3$		1.641 (0.002)	{FP=N 118.7 (0.1) CP=N 104.3 (0.1)	»	108
$(C_6H_5)_3P{=}NR$ ("pale-green substance")	ditto	1.630 (0.005)	CP=N 110	»	109
$(C_6H_5)_3P{=}NR$ ("brown substance")	»	1.56 (0.02)	CP=N 112 (3)	»	110
IV. P=O bond					
$(CH_3)_3PO$		1.479	CP=O 112.3	e.d.	111
$(CH_3)_2P(O)OH$	ditto	1.495 (0.005)	{CP=O 111.5 (0.5) OP=O 112.7 (0.2)	X-ray	112
$(CH_3)_2NPO(C_6H_5)_2$	»	1.47	CP=O 117.6	ditto	113
$(C_6H_5)_2P(O)OH$	»	1.45	CP=O 111	»	114
$R-PO(OCH_3)_2$ R = hydrocarbon rings	»	1.473 (0.008)	{CP=O 114.0 (1.0) OP=O (mean)	»	115
 where n = 8,9,11 or 12)					
$PO(NH_2)_3$	»	1.510 (0.003)	NP=O 112 (mean)	»	116
$\{PO[N(CH_3)_2]_2\}_2C_4H_4$	»	1.476 (0.004)	{NP=O 112.0 CP=O 110.9	»	117
$(HO)_3PO$	»	1.52 (0.03)	OP=O 113	»	118
$(HO)_3PO \cdot {}^1/_2H_2O$	»	1.490 (0.005)	OP=O 111.8 (0.3)	»	119
$HP(OH)_2O$	»	1.47 (0.03)	OP=O 115	»	120
$(ClC_6H_4O)_2PO(OH)$	»	1.497 (0.009)	OP=O 112 (mean)	»	121
$(C_6H_5CH_2O)_2PO(OH)$	»	1.47 (0.01)	OP=O 113 (mean)	»	122
$(C_6H_4NO_2)_3PO_4$	»	1.438 (0.005)	OP=O 115 (mean)	»	123
$(C_6H_5O)_3PO$	»	1.432 (0.01)	OP=O 115 (mean)	»	124
POF_3	»	1.436 (0.006)	FP=O 117.0 (0.2)	e.d.	127
$HPOF_2$	»	1.437 (0.006)	{HP=O 117.9 (2.0) FP=O 116.3 (1.0)	m.w.	126
$POCl_3$	»	1.449 (0.005)	ClP=O 114.7 (0.2)	e.d.	127
CH_3POCl_2	»	1.448 (0.005)	{ClP=O 114.5 (0.5) CP=O 117.4 (1.0)	ditto	128
$C_6H_5POCl_2$	»	1.47 (0.01)	{ClP=O 116 (1) CP=O 116 (2)	»	129
$(CH_3)_2NPOCl_2$	»	1.47 (0.02)	ClP=O 116	»	72
$POBr_3$	»	1.442 (0.02)	BrP=O 115 (2)	X-ray	130

Table 3 (continued).

Formula	Bond type	r (P=X), Å	YP = X angle, deg	Method of investigation	References
$POBr_3$	$-\overset{\vert}{\underset{\vert}{P}}=O$	1.41 (0.07)	—	e.d.	131
$(CH_3)_3PO \cdot SbCl_5$	ditto	1.56 (0.04)	—	X-ray	132
$[(C_6H_5)_2PO \cdot SeOCl_2]_2$	»	1.51 (0.01)	OP=O 112	»	133
$POCl_3 \cdot SbCl_5$	»	1.46 (0.02)	OP=O 111.5 (0.7)	»	132
$POCl_3 \cdot NbCl_5$	»	1.45 (0.02)	—	»	132
		V. P=S bond			
$C_2H_5)_3PS$	$-\overset{\vert}{\underset{\vert}{P}}=S$	1.86 (0.03)	CP=S 112	»	134
$(CH_3)_4P_2S_2$	ditto	1.96	{CP=S 115 PP=S 113	»	135
$(C_2H_5)_4P_2S_2$	»	1.94 (0.01)	{CP=S 115.0 (1.0) PP=S 112.8 (1.0)	»	136
$(CH_3)_2(C_6H_5)_2P_2S_2$	»	1.98 (0.02)	CP=S 115 (mean)	»	137
$[(C_2H_5)_2P(S)Se]_2$	»	1.932 (0.01)	{CP=S 117.0 (0.5) SeP=S 104.1 (0.5)	»	138
$[(C_2H_5)_2P(S)Se]_2Te$	»	1.926 (0.01)	{CP=S 116.0 (1.0) SeP=S 103.8 (0.6)	»	139
$(C_6H_5)_2P(S)OCH_3$	»	1.936 (0.006)	{OP=S 115.6 (0.4) CP=S 113.9 (0.8)	»	140
$(NH_2)_2P(S)\diagdown N-CH_3$ $NHCH_3(NH_2)P(S)\diagup$	»	1.958 (0.005)	NP=S 112 (mean)	»	141
$P(S)[N(CH_2)_2]_3$	»	1.910 (0.015)	NP=S 118.0 (1.5)	»	142
$[(CH_3O)_2PS_2]_2Te$	»	1.923 (0.007)	{OP=S 117.0 (0.3) SP=S 107.0 (0.3)	»	143
PSF_3	»	1.87 (0.03)	—	e.d./m.w.	125
PSF_3	»	1.87	—	m.w.	144
PSF_3	»	1.85 (0.02)	—	e.d.	145
$PSCl_3$	»	1.885 (0.005)	ClP=S 116.6 (0.2)	ditto	127
$PSBr_3$	»	1.890 (0.06)	—	»	131
$2(C_6H_5)_3PS \cdot 3I_2$	»	2.01 (0.03)	CP=S 113	X-ray	146
		VI. P=Se bond			
$[(C_2H_5)_2PSe_2]_2Se$	$-\overset{\vert}{\underset{\vert}{P}}=Se$	2.095 (0.006)	{CP=Se 116.6 (1.0) SeP=Se 103.1 (0.3)	ditto	147
$(C_6H_5)_2P(Se)OCH_3$	ditto	2.081 (0.008)	{CP=Se 114.2 (0.9) OP=Se 115.9 (0.6)	»	140
$[(C_6H_5)_3P(Se) \cdot HgCl_2]_2$	»	2.169 (0.006)	CP=Se 110.0 (0.4)	»	148

B. Single bonds

Formula	Bond type	r (PY), Å	YPY angle, deg	Method of investigation	References
		I. PH bond			
$HPOF_2$	$=\overset{\vert}{\underset{\vert}{P}}-H$	1.387 (0.01)	HPF 101.9 (1.5)	m.w.	126
$HF_2P \cdot BH_3$	$\leftarrow\overset{\vert}{\underset{\vert}{P}}-H$	1.409 (0.004)	HPF 98.6 (0.3)	ditto	93
		II. PC bond			
$(CH_3)_3PO$	$=\overset{\vert}{\underset{\vert}{P}}-\overset{\vert}{\underset{\vert}{C}}-$	1.813	CPC 106	e.d.	111
$(CH_3)_2P(O)OH$	ditto	1.780 (0.006)	CPC 107.3 (0.3)	X-ray	112
CH_3POCl_2	»	1.80 (0.025)	CPCl 103.3 (0.5)	e.d.	128
$(CH_3)_4P_2 \cdot 2BH_3$	$\leftarrow\overset{\vert}{\underset{\vert}{P}}-\overset{\vert}{\underset{\vert}{C}}-$	1.827 (0.010)	{CPC 106.0 (0.6) PPC 104.4 (1.0)	X-ray	97
$(CH_3)_4P_2S_2$	$=\overset{\vert}{\underset{\vert}{P}}-\overset{\vert}{\underset{\vert}{C}}-$	1.74	{CPC 105 PPC 105	ditto	135
$(CH_3)_2(C_6H_5)_2P_2S_2$	$=\overset{\vert}{\underset{\vert}{P}}-C\diagup$ $=\overset{\vert}{\underset{\vert}{P}}-\overset{\vert}{\underset{\vert}{C}}-$	1.82 (0.02) 1.88 (0.02)		»	137
$(C_2H_5)_3P \cdot CS_2$	ditto	1.82 (0.03)		»	106
$(C_2H_5)_3PS$	»	1.87 (0.04)	CPC 107	»	134
$(C_2H_5)_4P_2S_2$	»	1.83 (0.02)	{CPC 107.3 (1.0) PPC 102.2 (1.0)	»	136
$[(C_2H_5)_2P(S)Se]_2$	»	1.83 (0.04)	{CPC 105 SePC 105	»	138
$[(C_2H_5)_2P(S)Se]_2Te$	»	1.82 (0.04)	{CPC 103.9 (2.0) SePC 108.5 (1.5)	»	139
$[(C_2H_5)_2PSe_2]_2Se$	»	1.825 (0.03)	{CPC 103.3 (1.8) SePC 108.5 (1.0)	»	147
$R-PO(OCH_3)_2$ (for R, see Table 3A)	$=\overset{\vert}{\underset{\vert}{P}}-\overset{\vert}{\underset{\vert}{C}}-_{ring}$	1.834 (0.009)	CPO 106.0 (mean)	»	115
$(C_6H_5)_3P=C=C=S$	$=\overset{\vert}{\underset{\vert}{P}}-C\diagup$	1.795 (0.007)	CPC 108.1 (0.4)	»	100
$(C_6H_5)_3P=C=C=O$	ditto	1.805 (0.006)	CPC 107.3 (0.3)	»	99

Table 3 (continued).

Formula	Bond type	r (PY), Å	YPY, angle, deg	Method of investigation	References
$(C_6H_5)_3P=C(Cl)-C(=O)C_6H_5$	$=P-C<$	1.81 (0.02)	—	»	103
$(C_6H_5)_3P=CH-SO_2-O-C_6H_4CH_3$	ditto	1.81 (0.02)	CPC 112 (mean)	»	102
$(C_6H_5)_3P=R$ ("dark-green substance")	»	1.81 (0.02)	CPC 108	»	105
$(C_6H_5)_3P=R=P(C_6H_5)_3$ ("pale-blue substance")	»	1.816 (0.015)	approx. tetrahedral val. angles at P	»	104
$(C_6H_5)_3P=CH_2$	»	1.823 (0.01)	CPC 105.0	»	98
$(C_6H_5)_3P=C(CH_2O_2C)-C(CO_2CH_3)=N-C_6H_4Br$	»	1.83 (0.025)			101
$(C_6H_5)_3P=C<^{P(C_6H_5)_3}_{C(CF_3)_2}>O$	»	1.85 (0.02)	CPC 104.4 (mean)	»	107
$(C_6H_5)_3P=NR$ ("pale-green substance")	»	1.792 (0.007)	CPC 109	»	109
$(C_6H_5)_3P=NR$ ("brown substance")	»	1.809 (0.012)	CPC 107 (3)	»	110
$F(C_6H_5)_2P=NCH_3$	»	1.806 (0.003)	CPC 107.1 (0.1)	»	108
$(CH_3)_2N(C_6H_5)_2PO$	»	1.805	CPC 105 (mean)	»	113
$HO(C_6H_5)_2PO$	»	1.81 (0.03)	CPC 108	»	114
$\{PO[N(CH_3)_2]_2\}_2C_4H_4$	$=P-C<$	1.809 (0.005)	NPC 107.2	»	117
$C_6H_5POCl_2$	$=P-C<$	1.76 (0.02)	—	e.d.	129
$(C_6H_5)_2P(S)OCH_3$	ditto	1.81 (0.02)	{CPC 105.7 (0.7) OPC 103.2 (1.0)	X-ray	140
$(C_6H_5)_2P(Se)OCH_3$	»	1.81 (0.03)	{CPC 104.8 (1.2) OPC 103.0 (1.7)	ditto	140
$(CH_3)_3PO\cdot SbCl_5$	$=P-C-$	1.81 (0.08)	CPC 109	»	132
$[(C_6H_5)_3PO\cdot SeOCl_2]_2$	$=P-C<$	1.80 (0.01)	CPC 107	»	133
$2(C_6H_5)_3PS\cdot 3I_2$	ditto	1.82 (mean)	CPC 106	»	146
$[(C_6H_5)_3P(Se)\cdot HgCl_2]_2$	»	1.81 (0.02)	CPC 109	»	148
		III. PN bond			
$(NH_2)_3P\cdot BH_3$	$\leftarrow P-N<$	1.653 (0.01)	NPN 108 (mean)	»	95
$PO(NH_2)_3$	$=P-N<$	1.656 (0.01)	NPN 106.5 (mean)	»	116
$(NH_2)_2P(S)-N(P)-P(S)(NHCH_3)NH_2$	$=P-N<$	{1.65 (0.02) 1.708 (0.015)	NPN 107 (2)	»	141
$PS[N(CH_3)_2]_3$	$=P-N<$	1.64 (0.02)	NPN 100.0 (1.5)	»	142
$\{PO[N(CH_3)_2]_2\}_2C_4H_4$	$=P-N<$	1.647 (0.006)	{NPN 106.9 CPN 107.2	»	117
$(CH_3)_2NPO(C_6H_5)_2$	»	1.67		»	113
$(CH_3)_2NPOCl_2$	»	1.67 (0.04)	ClPN 102 (1)	e.d.	72
$(CH_3)_2NPF_2\cdot B_4H_8$	$\leftarrow P-N<$	1.593 (0.006)	FPN 105 (2)	X-ray	96
		IV. PO Bond			
$(HO)_3PO$	$=P-O-$	1.57 (0.03)	OPO 106	ditto	118
$(HO)_3PO\cdot{}^1/_2H_2O$	ditto	1.552 (0.006)	OPO 107 (3)	»	119
$(C_6H_5O)_3PO$	»	1.567 (0.023)	OPO 100	»	124
$(C_6H_4NO_2)_3PO_4$	»	1.572 (0.005)	OPO 103.1	»	123
$(C_6H_5CH_2O)_2P(O)OH$	»	{1.555 (0.01) (P—OR) 1.545 (0.01) (P—OH)	OPO 105	»	122
$(ClC_6H_4O)_2P(O)OH$	»	1.497(0.009) (mean)	OPO 108	»	121
$HPO(OH)_2$	»	1.54 (0.03)	OPO 102	»	120
$(CH_3)_2P(O)OH$	»	1.559 (0.005)	OPC 107 (2)	»	112
$(C_6H_5)_2P(S)OCH_3$	»	1.60 (0.02)	OPC 103.2 (1.0)	»	140
$(C_6H_5)_2P(Se)OCH_3$	»	1.61 (0.03)	OPC 103.0 (1.0)	»	140
$[(CH_3O)_2PS_2]_2Te$	»	1.58 (0.02)		»	143
$(CH_3O)_2P(O)R$ (For R see Table 3A)	»	1.572 (0.010)	OPO 102.7 (0.4)	»	115
		V. PF bond			
$PF_3\cdot BH_3$	$\leftarrow P-F$	1.538 (0.008)	FPF 99.8 (1.0)	m.w.	92
$PF_3\cdot B_4F_6$	ditto	1.510 (0.015)	FPF 101.7 (1.0)	X-ray	94
POF_3		1.524 (0.003)	FPF 101.3 (0.2)	e.d.	127
PSF_3	$=P-F$	1.53 (0.02)	FPF 100.3 (2.0)	e.d./m.w.	125
$HF_2P\cdot BH_3$		1.552 (0.006)	FPF 100.0 (0.5)	m.w.	93
$HPOF_2$	ditto	1.539 (0.003)	FPF 99.8 (0.5)	ditto	126
	»	1.583 (0.005)	FPF 96.4 (0.3)	X-ray	96
	»	1.488 (0.002)	FPC 110.7 (0.1)	ditto	108

Table 3 (continued).

Formula	Bond type	r (PY), Å	YPY angle, deg	Method of investigation	References
		VI. PP bond			
$(CH_3)_4P_2 \cdot 2BH_3$		2.205 (0.005)	PPC 104.4 (1.0)	X-ray	97
$(CH_3)_4P_2S_2$		2.18	PPC 105	ditto	135
$(C_2H_5)_4P_2S_2$	ditto	2.22 (0.01)	PPC 102.2	»	136
$(CH_3)_2(C_6H_5)_2P_2S_2$	»	2.21 (0.02)	PPC 103.5	»	137
		VII. PS bond			
$[(CH_3O)_2PS_2]_2Te$		2.09 (0.01)		»	143
		VIII. PCl bond			
$POCl_3$		1.993 (0.003)	ClPCl 103.3 (0.2)	e.d.	127
$PSCl_3$	ditto	2.011 (0.003)	ClPCl 101.8 (0.2)	»	127
CH_3POCl_2	»	2.032 (0.009)	ClPCl 101.8 (0.5)	»	128
$C_6H_5POCl_2$	»	2.025 (0.005)	ClPCl 102 (2)	»	129
$(CH_3)_2NPOCl_2$	»	2.033 (0.008)	ClPCl 102 (1)	»	72
$POCl_3 \cdot SbCl_5$	»	1.96 (0.01)	ClPCl 106.5 (0.4)	X-ray	132
$POCl_3 \cdot NbCl_5$	»	1.94 (0.01)		ditto	132
		IX. PSe bond			
$[(C_2H_5)_2P(S)Se]_2$		2.275 (0.011)	SePC 107	»	138
$[(C_2H_5)_2P(S)Se]_2Te$	ditto	2.258 (0.01)	SePC 108.5 (1.5)	»	169
$[(C_2H_5)_2PSe_2]_2Se$	»	2.239 (0.007)	SePC 108.5 (1.0)	»	147
		X. PBr bond			
$POBr_3$		2.14 (0.01)	BrPBr 107 (mean)	»	130
$POBr_3$	ditto	2.06 (0.03)	BrPBr 108 (3)	e.d	131
$PSBr_3$	»	2.13 (0.03)	BrPBr 106.3	ditto	131

According to Raman spectra [149], in the gas phase the pentachloride also dissociates $PCl_5 \rightarrow PcL_3 + Cl_2$, to an extent which is determined by the temperature and pressure.

Table 4. Bond lengths in acyclic compounds of pentacoordinate phosphorus.

Formula	r (Pc), Å		r (P—Hal), Å		Method of investigation	Refs.
	axial	equatorial	axial	equatorial		
$P(C_6H_5)_5$	1.987 (0.006)	1.850 (0.02)	—	—	X-ray	169
$(CH_3)_2PF_3$	—	1.798 (0.004)	1.643 (0.003)	1.553 (0.006)	e.d.	162
CH_3PF_4	—	1.780 (0.005)	1.612 (0.004)	1.543 (0.004)	ditto	162
HPF_4	—	—	1.594 (0.005)	1.55 (0.03)	m.w.	158
PF_5	—	—	1.577 (0.005)	1.534 (0.004)	e.d.	170
PF_3Cl_2	—	—	(2.05 ± ±0.03)	(1.59 ± ±0.03)	ditto	77
PCl_5	—	—	2.124 (0.009)	2.020 (0.007)	»	171

In the gas phase the molecules of PF_5, PCl_5, and their derivatives have the configuration of a regular (D_{3h} symmetry) or nearly regular trigonal bipyramid. An empirical rule, according to which the more electronegative or a large series of substituents occupy axial positions in this configuration, was established on the basis of NMR, infrared, and Raman spectroscopic data [12,13]. There are no exceptions to this rule for acyclic structures, at least in the gas phase§.

§ Analysis of the vibrational spectra [150,151], measurements of the dipole moments [151,152], and also NQR and NMR data [153] show that the molecules of all the members of the PCl_nF_{5-n} series exist in the trigonal-bipyramidal configuration with the F atoms in the axial positions. The vibrational spectra of CF_3PCl_4 [154] and $(CF_3)_2PCl_3$ [155] and the ^{19}F NMR spectra of CF_3PCl_3F [156] show that the more electronegative $-CF_3-$ groups (compared with chlorine) are also in the axial positions. The trigonal-bipyramidal structure of the HPF_4 molecule with an equatorial H atom has been established from infrared [157] and microwave spectra [158]. Finally, the validity of the above rule is confirmed by the vibrational spectra of compounds in the series CH_3PF_4, [159] CCl_4PF_4, [160] and CF_3PF_4, [161] according to which the CX_3 groups are localised in the equatorial positions (C_{2V} symmetry). For the methyl derivatives CH_3PF_4 and $(CH_3)_2PF_3$, this was also found by electron diffraction [162].

However, there is a divergence in views concerning CF_3PF_4. Thus in a microwave study [163] it was asserted that the CF_3 group occupies an axial position (C_{3V} symmetry). However, no details of the structure are quoted and the authors do not exclude the possibility of the presence of conformations other than C_{3V}. Earlier an axially substituted model of the CF_3PF_4 molecule was preferred on the basis of NMR spectra [12].

Some evidence for the possibility of the existence of conformational isomers in the case of the CF_3PF_4 molecule (together with the basic structure having the C_{2V} symmetry) was noted in the interpretation of the vibrational spectra [161].

According to electron-diffraction data (Table 4), the non-equivalence of the axial and equatorial bonds increases from 0.043 ± 0.008 Å in PF_5 to 0.104 ± 0.01 Å in PCl_5. It has also been established that, with increase of the number of CH_3 substituents, there is an increase in the length of both axial and equatorial P–F bonds, the length of the axial bond increasing faster. Therefore, on the basis of a calculation of the ratio of the lengths of the P–F axial bonds in PF_5 (adopted as unity by convention) and in substituted fluorophosphoranes, the ionic structure $[R_4P]^+F^-$ was proposed[164] for $(CH_3)_4PF$. However, there is so far no evidence for the existence of ionic structures of pentacoordinate phosphorus fluorides comparable to those found in the chlorides[165-168]. The mixed halide PF_3Cl_2 was investigated by electron diffraction as early as the end of the 1930's. It was established that the F atoms are equivalent and are therefore in the equatorial positions, but the lengths of the P–F (1.59 Å) and P–Cl (2.05 Å). bonds found throw doubt on the correctness of this conclusion. The vibrational spectra indicate that both axial positions in PF_3Cl_2 are occupied by F atoms[13,150]. The general tendency is probably as follows: the lengths of the axial bonds in the trigonal-bipyramidal structures vary approximately between the same limits as the lengths of the corresponding bonds of tricoordinate phosphorus; the lengths of the equatorial bonds are closer to those of single tetracoordinate phosphorus bonds (Table 1).

V. INTERNAL ROTATION AND CONFORMATIONAL ISOMERISM IN ACYCLIC ORGANOPHOSPHORUS COMPOUNDS

The study of intramolecular rotation and conformational isomerism has recently become a central problem in the theory of chemical structure. However, the only possible realistic approach to this problem still consists in the accumulation and analysis of experimental data. There are no general approximate hypotheses which would account for the characteristics of intramolecular rotation. The applicability of each of the numerous empirical methods of calculation of potential barriers is limited to special cases, since these methods do not have a rigorous physical basis. In many cases the geometry of stable conformations of organophosphorus compounds can be satisfactorily accounted for by the mutual repulsion of the non-bonded atoms in the molecule. Owing to the considerable differences between the types of intermolecular interactions, the ratio of the rotational isomers in the mixture may be various depending on the state of aggregation of the substance.

1. Compounds with a P–B bond

An ethane-like staggered conformation, corresponding to minimum steric interactions, is characteristic of compounds of the type $X_3P.BY_3$ [X = H, F, $N(CH_3)_2$; Y = H] in the vapour (according to microwave data[92,93]) and in the crystalline phase (according to vibrational spectra[172] and X-ray diffraction[95]). The barrier to internal rotation (V_3) is 3.24 ± 0.15 kcal mole^{-1} in the $F_3P.BH_3$ molecule[92] and about 3.6–4.5 kcal mole^{-1} in the $HF_2P.BH_3$ molecule[93], i.e. is close to the value in ethane.

2. Compounds with a P–C bond

In the molecules of methylphosphines $P(CH_3)_3$ and $PH(CH_3)_2$ in the vapour phase, the mutual orientation of the methyl groups is also staggered and $V \leqslant 1$ kcal mole^{-1} according to electron diffraction data[56,63] and 2.6 ± 0.5 kcal mole^{-1} according to microwave data[59,62]. Microwave data show that the barriers to rotation in CH_3PH_2 (about 2 kcal mole^{-1}) [55] and CF_3PH_2 (2.36 ± 0.08 kcal mole^{-1}) [57] are approximately the same.

An electron diffraction study of $P(C_3H_5)_3$ vapour[70] showed that the deviation of each of the three cyclopropyl groups from its position in the staggered configuration with C_{3V} symmetry is different (9.5°, −13°, −15°) and "the attempt to interpret the data using the hypothesis that a mixture of molecules with different conformations is present proved fruitless".

Crystalline triphenylphosphine $P(C_6H_5)_3$ was shown by X-ray diffraction[65] to have the C_3 propeller-like conformation with angles between normals to the plane of the base of the phosphorus pyramid and to the plane of the phenyl rings of the order of 60°. In the vapour phase the $(CH_3)_3PO$ molecule[111] has the C_{3V} symmetry with the *trans*-disposition of H atoms relative to the oxygen atom.

Vibration spectra[173] showed that in the liquid phase the more complex structures $CH_2YP(=O)X_2$ (X = F or Cl; Y = Cl, CH_3, or CH_2Cl) exist as mixtures of *trans*- and gauche-conformers with C_S and C_1 symmetry.

In the solid phase of the fluorides, conformers with the C_1 symmetry remain, while in the solid phase of the chlorides the remaining conformers have the higher C_S symmetry.

An electron diffraction study of the vapour of $C_6H_5P(=O)Cl_2$ showed[129] that the most probable conformation of this compound involves a coplanar disposition of the phenyl ring and the P=O bond. This conformation corresponds to minimum steric interaction. Here the barrier to rotation about the P–C bond is approximately 1 kcal mole^{-1}.

The internal rotation of CH_3 groups in the molecules of the pentacoordinate phosphorus compounds CH_3PF_4 and $(CH_3)_2PF_3$ could not be characterised by electron diffraction[162]. The barrier to rotation in CH_3PF_4 is very low (about 10 cal mole^{-1}), which leads to the hypothesis of free rotation. At the same time the barrier to internal rotation in the CF_3PF_4 molecule is 5.0 ± 1.5 kcal mole^{-1} according to microwave data[183].

3. Compounds with a P–N bond

According to low-temperature NMR spectra[174-178], the usual barrier to rotation relative to the P–N bond in the series of aminophosphines $R_1R_2NPR_3R_4$ ($R_1 = CH_3$; R_2 = H, CH_3, or $C_6H_5CH_2$; R_3 = Cl, C_6H_5, or CF_3; R_4 = Cl, C_6H_5, or CF_3) varies in the range from about 9 to 14 kcal mole^{-1}¶. This value is higher than for P–B and P–C bonds (see above). It has also been shown[174] that, particularly in aminophosphines with geminal substitution at the phosphorus atom ($R_3 = R_4$ = Cl or C_6H_5), the barrier depends on the dimensions of the R_1 and R_2 substituents linked to the nitrogen atom. When one of the substituents has a branched chain (for example, $R_1 = C_6H_5CH_2$ and $R_2 = CH_3$), the barrier is higher by 2–3 kcal mole^{-1} (up to about 14 kcal mole^{-1}) than for $R_1 = R_2 = CH_3$ (about 11 kcal mole^{-1}).

Recent studies indicate the possibility of rotational isomerism relative to the P–N bond in compounds with

¶ According to an estimate based on infrared spectra[179], in the compound $CH_3NH-P(CF_3)_2$ the barrier to internal rotation is about 20 kcal mole^{-1}. However, this value is disputed in another study[176].

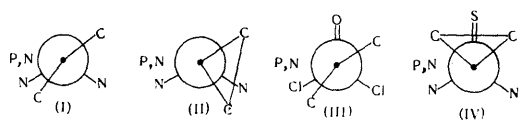
tricoordinate phosphorus[179,180]. This possibility follows in particular from the NMR spectra[180] of the compound $C_6H_{12}NPF_2$. The existence of two *gauche*-isomers has been postulated on the basis of infrared spectra[179] for the compound $CH_3NH-P(CF_3)_2$ in the gas phase, in the liquid, and in benzene solution: the first with a hydrogen atom and the second (in a smaller amount) with a methyl group between CF_3 groups; in this case free rotation obtains at temperatures above 88°C. However, the authors of the investigation[176] believe that in the latter case the characteristics of the infrared spectra cannot be interpreted similarly, i.e. in the sense of the existence of a mixture of isomers. They found that *N*-deuterated specimens $CH_3ND-P(CF_3)_2$ contains two isomers in proportions of 4:1 only below −120°C and on the basis of steric considerations it was postulated that the isomer with the deuterium atom between the CF_3 groups should predominate.

The problem of the energy favouring a particular conformer is controversial. As in the examples examined above, on the basis of NMR spectra[180] preference is given to the *gauche*-conformation of $C_6H_5(CH_3)NPF_2$ as the more favourable. The same conformation was found by X-ray diffraction for the $(CH_3)_2NPF_2$ molecule[73].

At the same time the authors of one of the NMR investigations[174] assert that at least symmetrically substituted aminophosphines $(CH_3)_2NP(C_6H_5)_2$ and $(CH_3)_2NPCl_2$ exist in the sterically less favourable *anti*-conformation. This conclusion was disproved by another NMR study[176] in which preference was given to the *gauche*-conformation of the $(CH_3)_2NPCl_2$ molecule.

On the other hand, electron diffraction showed that in the vapour phase $(CH_3)_2NPCl_2$ has the *anti*-conformation. Moreover, the *anti*-conformation is the most stable in the case of diphosphines (see below) and hydrazine derivatives.

The rotational forms of the $P[N(CH_3)_2]_3$ and $P[N(CH_2)_2]_3$ molecules in the vapour phase found by electron diffraction[71],

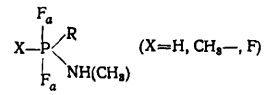


are also not the most favourable from the standpoint of steric interactions (models I and II).

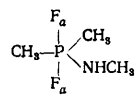
There are comparatively few experimental data for compounds of tetracoordinate phosphorus. Electron diffraction showed[72] that in the vapour phase the $(CH_3)_2NP(=O)Cl_2$ molecules has an asymmetric conformation (model III), the existence of which are confirmed by NQR spectra[181]. On the other hand, X-ray diffraction showed[142] that the $P(=S)[N(CH_2)_2]_3$ molecule has a conformation close to C_{3V} (model IV).

Vibrational spectra demonstrated[182-184] that the monosubstituted amides $RNHP(=S)Cl_2$ exist as mixtures of two rotational isomers in the liquid phase and in solutions. Under these conditions, the disubstituted amides $R_2NP(=S).Cl_2$ exist in a single conformation[182]. It has been noted that the presence of only one isomeric form of $R_2NP(=S)Cl_2$ cannot be explained by steric hindrance to the rotation of the R_2N group about the P–N bond. The geometrical parameters of the fragments about the nitrogen atom in di- and mono-substituted amides are close in magnitude and therefore the steric hindrance should be approximately the same.

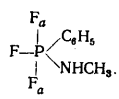
The barriers to the rotation of $NHCH_3$ groups in compounds of pentacoordinate phosphorus of the type



were determined from NMR spectra[185,186]. They vary from 5.0 ± 1.5 kcal mole^{-1} in



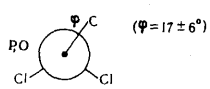
to 12 ± 1.0 kcal mole^{-1} in



These high values are attributed to the existence of intramolecular hydrogen bonds between the $NHCH_3$ groups and one of the axial F_a atoms, as shown by the observed nonequivalence of F_a atoms.

4. Compounds with a P–O bond

Only one conformer of the CH_3OPCl_2 molecule in the vapour and liquid phases with the C_S symmetry was found from vibrational spectra[187]. The barrier to rotation is 1.0 kcal mole^{-1} (1.6 kcal mole^{-1} for the deuterated derivative). It proved impossible to make a choice between the two possible orientations of the methoxy-group. According to electron diffraction data[75], the statistical mean conformation of this molecule in the vapour phase is somewhat distorted relative to C_S:



and is close to the form more favourable from the standpoint of steric interactions.

It follows from the vibrational spectra[188] of $(CH_3O)_3P=S$ that at least two conformers exist in the liquid phase and only one in the crystalline phase. The structure of this molecule in the crystalline phase has not been investigated but X-ray diffraction showed[134] that $(C_2H_5)_3P=S$ has a conformation with C_3 symmetry and the angle $\varphi < 90°$ (see above). The vibrational spectra obtained for the compounds $ROP(=Y)X_2$ (R = CH_3 or C_2H_5; X = F or Cl; Y = O or S) in the vapour, liquid, and solid phases and in solutions[189-194] indicate the presence of at least two conformers in all cases. The specific conformations were not established on the basis of the spectra but it is suggested that one of them has the C_S symmetry.

It has been shown[194] that, on the assumption of the occurrence of attraction (but not repulsion) between the CH_3 group and the Cl and S atoms, it is possible to select two models ($\varphi = 0°$ and $\varphi = 120°$) for the $CH_3OP(S)Cl_2$ molecule, whereupon the calculated frequencies agree with the experimental values for solutions of this substance.

5. Compounds with the P–P bond

From the standpoint of steric interactions, the *anti*-conformation (C_{2h} symmetry) and the *gauche*-conformation (C_2 symmetry) are the most probable for molecules of the type P_2X_4.[11] The halogeno-derivatives probably have the *anti*-conformation, which is the less favourable of the two. This has been demonstrated spectroscopically for P_2Cl_4 in all three phases[195]. Preference is also given to the *anti*-conformation of the P_2F_4 molecule[186]. The problem of the possible change in the conformation of the P_2I_4 molecule on passing from one phase to another was discussed for some time. C_{2h} symmetry was found for crystalline P_2I_4 from Raman spectra[197] and by X-ray diffraction[78]. At the same time measurements of the dipole moments[198] and interpretation of the infrared spectra[197,199] led to the assertion that, in contrast to the crystalline phase, in CS_2 solution this molecule has the C_2 symmetry. However, a subsequent repetition of the spectroscopic study[200] showed that P_2I_4 retains the C_{2h} symmetry also in CS_2 solution and an anomaly in the infrared spectra of the solutions was explained[201] by the equilibrium $3P_2I_4 \rightleftharpoons 4PI_3 + \frac{1}{2}P_4$.

The vibrational spectra of P_2H_4 in the vapour, liquid, and solid phases[202-204] have nevertheless been interpreted on the basis of the *gauche*-conformation. The spectrum of the liquid phase[203] was complicated by the presence of the decomposition products of the compound. At the same time the NMR spectrum[205] demonstrated the equivalence of the hydrogen atoms in P_2H_4. Although the author of the investigation interprets this phenomenon as evidence for rapid interconversion of different conformers, it is also consistent with the possible existence of fixed *anti*- or eclipsed (*cis*-) conformations.

Interpretation of the infrared spectra of $P_2(CH_3)_4$ showed[206] that only the *anti*-conformation exists in the crystalline phase, while in the liquid phase both *anti*- and *gauche*-conformers are present. It proved impossible to arrive at any conclusion concerning the conformation of this molecule in the gas phase. The ^1H NMR spectra[207] of the liquid phase of $P_2(CH_3)_4$ are inconsistent with the existence of the *anti*-conformer.

The *trans*-conformation with C_{2h} symmetry has been found for a number of structures of the type $R_4P_2(=S)_2$ (R = CH_3, C_2H_5, or C_6H_5) in both the crystalline phase (by X-ray diffraction[135-137] and from infrared spectra[208-212]) and in the liquid phase and in dilute solution (from infrared spectra[212]). Certain differences between the spectra of diphosphine disulphides in the crystalline and liquid phases are attributed[11] to the possibility of hindered rotation about the P–C bonds. However, three conformations of $(CH_3)_4P_2 \cdot 2BH_3$ were found in the most stable of the crystalline modifications of this substance[97].

6. "Pseudorotation" in Compounds of Pentacoordinate Phosphorus

The NMR spectra of phosphorus pentafluoride (PF_5) and a number of its derivatives $PX_{5-n}F_n$ are evidence of the equivalence of the F nuclei in these compounds[12-16,213]. In particular, the equivalence in the compounds PXF_4 might correspond to an actual equilibrium configuration of the type of a tetragonal pyramid with C_{4v} symmetry. However, as already mentioned above, only the trigonal-bipyramidal configuration is characteristic of compounds of pentacoordinate phosphorus.

To account for the effect observed in the NMR spectra, the concept of "pseudorotation"—an intramolecular process as a result of which two equatorial atoms are transferred to axial positions and conversely—has been resorted to[15,16,214]. The process is accompanied by a deformation of the valence angles:

As a result, the initial trigonal bipyramid is rotated by 90° relative to the equatorial bond distinguished in the diagram. Such inversion is analogous in a certain sense to the inversion in the ammonia molecule[215] and may be caused by intramolecular vibrations[216]. Calculations yield the following values for the energy barrier to "pseudorotation" (kcal mole^{-1}): 7.6 for PF_5, 10.9 for $PClF_4$, 15.0 for CH_3PF_4, and 13.5 for PCl_5. A systematic analysis of the possible isomeric forms caused by "pseudorotation" in trigonal-bipyramidal molecules has been carried out[217].

At the same time it should be noted that the available data do not as yet allow an unambiguous determination of the true mechanism of the above intramolecular inversion. The Raman spectra obtained[218] for gaseous and liquid PF_5 do not prove the mechanism of this process as described above but they are not inconsistent with it either. In certain specific cases other possible mechanisms of such rearrangements have been postulated[16,219].

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The molecular structures of organophosphorus compounds have been examined in this review on the basis of the classical theory of structure. The aim was not to investigate the agreement between approximate electronic concepts, in particular the concept of $p_\pi - d_\pi$ interactions, and the characteristics of geometrical structure. This problem is complex and controversial[220] and requires special analysis.

The characteristics of the geometrical structure of molecules revealed by the analysis of experimental data permit the prediction of the structural parameters for compounds which have not yet been investigated and also make it possible to study the dependence of various properties of materials on their molecular structure.

Structural information is now available for organophosphorus compounds in which the phosphorus atom has different coordination numbers. The length of the phosphorus–element bond depends both on the valence state of the atoms involved in the bond and on the atoms in its immediate environment. The valence angles at the phosphorus atom are fairly characteristic of the given coordination number of phosphorus.

The characteristics of the molecular conformations determined by the rotation about the phosphorus–element bond are less well defined. Steric interactions play a considerable role but do not determine the conformation of the molecules in all cases.

ADDENDUM

After the review had been sent to the printers, a number of new studies on the structure of acyclic organophosphorus compounds were published. In many cases (concerning the reinvestigation of certain structures or more detailed reports with revision of earlier data) the appropriate corrections were introduced into the main text. In addition the following data merit consideration.

The electron diffraction study of the structure of tetramethyldiphosphine[221] $P_2(CH_3)_4$ evidently terminates the controversy concerning the most favourable conformation of this molecule (see above). In the gas phase $P_2(CH_3)_4$ was found to have a conformation close to the *anti*-form. The angle of deviation from the *anti*-form (16°) is less than the error in the determination of the angle in the above study (23°). Among other parameters found for the tetramethyldiphosphine molecule, we have the following:

$r(P\text{—}P) = 2.192\ (0.009)$ A, $\angle CPC = 99.6\ (1.0)°$,

$r(P\text{—}C) = 1.853\ (0.003)$ A, $\angle PPC = 101.1\ (0.7)°$.

The authors of the investigation note that the geometrical parameters of diphosphine are close to those found for their analogues—monophosphines (see, in particular, Table 2).

The vibrational spectra of $N[P(CF_3)_2]_3$ are inconsistent with the planar configuration of the NP_3 fragment and have been interpreted on the basis of its pyramidal structure[222]. The infrared spectrum of the compound in the vapour phase obtained somewhat earlier[223] apparently did not contradict the hypothesis that the NP_3 fragment is planar. However, it has been noted[222] that certain important frequencies were too weak, as a result of which many ambiguities remained. Since, as stated by Hendra et al.[222], conformational analysis did not confirm the planarity of the NP_3 fragment, additional infrared spectra and laser Raman spectra in the liquid phase were measured. The study of all the available spectra[222,223] showed that the nitrogen atom in the compound can indeed be regarded as located outside the P_3 plane. As the same time one cannot exclude the possibility of an equilibrium between the planar and pyramidal structures.

The authors believe that in the pyramidal configuration of the $N[P(CF_3)_2]_3$ molecule the role of the F atoms, despite their electron-accepting properties, is more likely to involve a weakening of the P—N bonds than their strengthening. In this connection it is interesting to recall that in the compound

$$(NH_2)_2P(S)\diagdown N\text{—}CH_3,\quad NH_2(NHCH_3)\,P(S)\diagup$$

investigated by X-ray diffraction in the crystalline phase[141], the length of the bonds between the P atoms and the central N atom is greater by 0.06 Å than that of the remaining $=P\text{—}N\diagup$ bonds. However, the central N atom has a planar bond configuration.

An X-ray diffraction study of the structure of triethynyl phosphine[224] $P(C{\equiv}CH)_3$ showed that in the crystalline phase this molecule has the C_{3v} symmetry. The mean values of the principal geometrical parameters are as follows: $r(P\text{—}C{\equiv}) = 1.75$ Å; $\angle CPC = 101°$. A characteristic feature is the non-linearity of the P—C≡C fragment (the angle of deviation from linearity reaches up to 11°). A similar effect was noted also in the structures $P(C{\equiv}C\text{—}C_6H_5)_3$ [68] and $P(C{\equiv}N)_3$, [69] investigated previously by X-ray diffraction.

Analysis of the infrared spectra obtained in all three phases is evidence of the presence of two rotational isomers with C_S symmetry in compounds of the series $(CF_3)_2PXY$ (where X = O or S and Y = H or D).[225]

An X-ray diffraction study of the structure of triphenylphosphine oxide[226] $(C_6H_5)_3P{=}O$ furnished a criterion allowing a quantitative estimation of the effect of the environment on the length of the bond of the type

$$=P\text{—}C\diagup$$

The length of this bond in the $(C_6H_5)_3P{=}O$ molecule is 1.76 (0.01) Å, i.e. the same as the value found by electron diffraction for the $C_6H_5P(=O)Cl_2$ molecule (see Table 3B). It is striking that the $=P\text{—}C\text{—}$ bond also remains unchanged, within the limits of experimental error, on passing from the $(CH_3)_3P{=}O$ molecule to $CH_3P(O)Cl_2$ (Table 3B). However, in the series

$$(C_6H_5)_3P{=}O \rightarrow (C_6H_5)_3P{=}NR \rightarrow (C_6H_5)_3P{=}C{=}C{=}X \rightarrow (C_6H_5)_3P{=}CH_2$$

the length of the $=P\text{—}C\diagup$ bond increases to 1.82 Å (Table 3B). The remaining parameters of the $(C_6H_5)_3P{=}O$ molecule have the following values:

$r(P{=}O) = 1.46(0.01)$ A, $\angle CPC = 107.1\ (0.7)°$, $\angle CP(=O) = 111.7\ (0.6)°$.

The length of the single P—S bond was determined for only the second time in an X-ray diffraction study of the structure of the $[(iso\text{-}C_3H_7O)_2PS_2]_2$ molecule[227]. In this molecule $r(-P{=}S) = 1.908\ (0.003)$ Å is shorter than $r(=P\text{—}S) = 2.072\ (0.002)$ Å by about 0.16 Å, i.e. by the same amount as in the $[(CH_3O)_2PS_2]_2Te$ molecule (Table 3). The remaining parameters found in this investigation[224] are as follows:

$r(=P\text{—}O) = 1.561\ (0.005)$ A,

$\angle OPO = 96.6\ (0.2)°$, $\angle OP{=}S = 119.3\ (0.2)°$,

$\angle SPO = 108.2\ (0.2)°$, $\angle SP{=}S = 104.8\ (0.1)°$.

The shortening of $r(-P{=}O)$ compared with $r(=P\text{—}O\text{—})$ found by an X-ray diffraction study of the structure of $(CH_3O)_2P(=O)R$ (where R = 3-hydroxy-2,2,5,5-tetramethyltetrahydrofuryl),[228] is only about 0.11 Å. The parameters of this structure are as follows:

$r(-P{=}O) = 1.471\ (0.007)$ A, $\angle OPO = 102.3\ (0.4)°$,

$r(=P\text{—}O\text{—}) = 1.581\ (0.009)$ A, $\angle OPC = 106.5\ (0.4)°$,

$r(=P\text{—}C\text{—}_{ring}) = 1.812\ (0.009)$ A, $\angle OP{=}O = 114.4\ (0.4)°$,

$\angle CP{=}O = 112.0\ (0.4)°$.

According to vibrational spectra[229], the $C_6H_5S\text{—}PF_4$ molecule has an equatorially substituted trigonal-bipyramidal structure.

An X-ray diffraction reinvestigation of the structure of $(CH_3)_4P_2S_2$ (see the data[135] in Table 3) showed[230] that the crystal unit cell of the substance contains two types of molecules with the following parameters:

	Molecule (I)	Molecule (II)
$r(=P\text{—}P=)$	2.245 (0.006) A	2.161 (0.004) A
$r(-P{=}S)$	1.951 (0.003) A	1.970 (0.004) A
$r(=P\text{—}C\text{—})$	1.800 (0.008) A	1.820 (0.008) A
$\angle CP{=}S$	115.0 (0.3)°	115.0 (0.3)°
$\angle PP{=}S$	111.0 (0.2)°	112.0 (0.2)°
$\angle CPC$	103.5 (0.4)°	105.3 (0.4)°.
$\angle PPC$	105.6 (0.3)°	104.3 (0.4)°.

The authors failed to find any cause of the observed differences between the bond lengths in molecules (I) and (II) other than the effect of steric factors.

An electron diffraction study showed[231] that in the gas phase the $(CH_3)_2NPF_2$ and H_2NPF_2 molecules have the *gauche*-conformation [the $(CH_3)_2NPF_2$ molecule has the *gauche*-conformation also in the crystalline phase[73]]. The following fundamental geometrical parameters of these molecules have been quoted:

	$(CH_3)_2NPF_2$	H_2NPF_2
$r(>P-F)$	1.589 (0.003) Å	1.581 (0.003) Å
$r(>P-N<)$	1.684 (0.008) Å	1.661 (0.007) Å
$\angle$ FPN	97 (4)°	101.0 (1.1)°
$\angle$ FPF	99 (3)°	95.3 (1.1)°

It was found that the configuration of the valence angles at the nitrogen atom in the above compound is non-planar in the gas phase (the sum of the valence angles is equal to 348.4° and 346° respectively), while in the crystalline phase the PNC_2 fragment in the $(CH_3)_2NPF_2$ molecule is planar. It was noted that in $(CH_3)_2NPF_2$ the P–N bond length found in the gas phase is higher by 0.056 Å than the value found in the crystalline phase, while the P–F bond length is smaller by 0.021 Å (Table 2).

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Thermal Stability of Cation-exchange Resins

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Experimental work on the thermal stability of cation-exchange resins in air, water, certain aqueous solutions, and also organic media is summarised for the first time. Conclusions are reached about the effect of various factors on the thrmal stability and about the nature of the processes responsible for the decrease in exchange capacity. Special attention is paid to the existence of an inherent relation between the thermal stability and the catalytic activity of ion-exchange materials. A list of 235 references is included.

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1. INTRODUCTION

The action of heat[1,2], radiation[3], and oxidants[4] on carbon-chain polymers often causes irreversible chemical changes in their macromolecules owing to rupture of the carbon–carbon single bond and the occurrence of degradation processes. Ion-exchange materials (resins and membranes) contain also the far less stable bonds between functional groups and the polymer matrix (carbon–nitrogen, carbon–sulphur, carbon–phosphorus, etc.). For this reason the main problem of the thermal, chemical, and radiation stability of ion-exchange materials is the behaviour of the functional groups, which are responsible for the ion-exchange and electrochemical properties under certain conditions.

The importance of this problem arises entirely from the inevitable heat-treatment of exchanger resins and membranes during their preparation and examination of their physicochemical properties. In several actual cases of practical exploitation, exchangers are subject simultaneously to thermal, chemical, and radiation effects.

At the high temperature of the polycondensation of hydroxybenzenesulphonic acid with formaldehyde the exchange capacity of the sulphonated cation-exchange resin may be diminished by desulphonation[5], the formation of sulphones, and the interaction of sulpho-groups with formaldehyde[6], and the three-dimensional structure of the polymer may undergo partial breakdown with oxidation of the degradation products by sulphuric acid[7]. In the preparation of sulphonated cation-exchange resins based on polystyrene and formaldehyde[8] or vinyl polymers[9] an excessive rise in temperature results in a decrease in the exchange capacity.

The drying of exchange resins, which is usually conducted at a high temperature (at or above 100°C) in order to determine their physicochemical properties[10,11], and their preparation for chromatographic separations[12-17] and for the production of heterogeneous membranes[18] may be accompanied by a diminution in the exchange capacity[10,18,19] and by irreversible changes in the structure of the three-dimensional network[20].

Many analytical separations by ion-exchange chromatography are conducted at high temperatures[21-29]. While utilising the kinetic and thermodynamic advantages which this confers, we must reduce to a minimum the chemical changes in the exchange resins that are inevitable with an incorrect choice of temperature conditions for the separation. The regeneration of spent exchangers is often accomplished by means of heated solutions[30-32], the consumption of which decreases with rise in temperature.

Exchangers are often used at high temperatures under industrial conditions, e.g. in the deionisation of industrial waters[33], the purification of radioactive solutions[34], and many catalytic reactions of organic compounds[35]. The correct choice of exchanger, necessarily taking into account its thermal, chemical, and radiation stability, will govern its useful life, and often the successful accomplishment of the desired processes. Thus practical interests demand a comprehensive investigation and survey of data on the thermal, chemical, and radiation stability of ion-exchange materials in all the typical media in which they are used. Results for the radiation stability of ion-exchange materials have been reported in detail in a monograph[36], but data on their thermal and chemical stability are now summarised for the first time.

2. METHODS FOR THE STUDY OF THE STABILITY OF ION-EXCHANGE MATERIALS

Ion-exchange materials are not individual compounds. Their composition and properties depend on the purity of the original monomers and the conditions for synthesis of the polymer, the content of low-molecular-weight compounds in the final product, and its pretreatment. The physicochemical properties are therefore determined on exchanger fractions of definite particle-size distribution, freed from impurities by acid[37-39] or alkali–acid[40-45] treatment, and in individual cases also by washing with organic solvents[46,47]. Ion-exchange membranes are usually prepared by similar methods[48,49], but the possibility of destroying the reinforcing fabric must be borne in mind[49].

Several physicochemical properties—exchange capacity, moisture capacity, relative swelling, density, etc.—must be studied for a complete description of exchangers and their stability, and with membranes the electrical conductivity, selectivity, permeability to water, mechanical strength, and elasticity must also be examined.

The most important physicochemical characteristic of ion-exchange materials is the total exchange capacity. In the case of polyfunctional exchangers and membranes the exchange capacity is also determined with respect to individual functional groups. However, by no means all methods described in the literature for estimating exchange capacity can be used to study the stability of exchangers and membranes. Many authors recommend statistical methods for determining the total exchange capacity of mono- and poly-functional exchangers in the hydrogen or the hydroxide form; these involve treating a weighed portion of the resin with excess of a standard solution of alkali [40,45] or acid [40,50,51] in a closed flask for a definite time. Sometimes a neutral salt is added to the solution to accelerate the exchange of mobile ions [39]. Total exchange capacity is not a happy choice to represent the stability of a polyfunctional exchanger, since different types of functional groups usually split off at different rates, and furthermore carboxylic and phenolic groups may be formed on irradiation or by the action of oxidants.

The most reliable measure of the resistance of an exchanger to a given factor is the capacity which is retained with respect to individual active groups (expressed in mg-equiv. g^{-1} initial resin or as a percentage of its original exchange capacity), determined potentiometrically [40,52-55], conductometrically [56,57], or titrimetrically [40,41]. Potentiometric methods require a large amount of time, and are advisable only for studying reaction mechanisms and the formation of new functional groups. In series of experiments it is more useful to apply rapid methods for the separate determination of the exchange capacity of cation-exchange resins in the hydrogen form [58,59] (direct titration of the resin in the presence of a neutral salt), for whose development much credit is due to Vasil'ev and his coworkers [60-66]. The considerable difficulties involved in the separate determination of the active groups of different strengths in phosphoric-acid cation-exchange resins [67] have not yet been overcome.

Complexometric methods [41,68], which do not require conversion of the exchanger into the hydrogen form, have undoubted advantages in estimating the exchange capacity of the salt forms of cation exchangers.

In laboratory practice, and sometimes also in studies of the stability of ion-exchange materials, use is quite often made of the static exchange capacity [40,49,69,70], which is determined by titrating a solution of a neutral salt, an acid, or an alkali in equilibrium with the test polyelectrolyte. The static exchange capacity depends on many factors—the concentration of the solution, the temperature, the degree of cross-linking of the exchanger, etc.—and therefore cannot serve as a criterion of its stability.

In the determination of the exchange capacity of an exchanger under dynamic conditions an electrolyte solution is filtered through a layer of the resin, and the ions displaced from the active groups are subsequently titrated in the filtrate [38,40,41,67,71]. This method is considerably more complicated than the static method, and requires a large consumption of reagents, but it gives valuable information on the dynamics of ion-exchange processes and on the properties of the exchangers.

Values obtained by the above methods for the exchange capacity may differ from those calculated from the formula of the structural unit, owing to incomplete sulphonation and phosphorylation or the occurrence of secondary processes which convert some of the functional groups into an "inactive" state [72-75]. The content of "inactive" sulphur or phosphorus is determined from the difference between the results of elementary analysis [76] and titration.

Exchange capacity is usually expressed in mg-equiv. g^{-1} dry material. This quantity is to some extent arbitrary, since it is evidently impracticable to obtain "absolutely" anhydrous exchangers without changing their chemical nature. Yet in several cases it is necessary to use dehydrated exchangers.

Conditions of dehydration must be chosen for each type of ion-exchange resin or membrane. It must be remembered that part of the bound water remains in the exchangers, and is capable of exerting a decisive effect on their behaviour towards radiation, heat, and reagents. It is interesting that the cation exchanger KU-2, after being dried at 100°C to constant weight, contains monohydrates of the sulpho-groups or ~ 9% water [77].

Many methods have been described for removing water from cation-exchange resins: these reduce to drying in a thermostat at 90°, [78] 95–100°, [79] 100 ± 50°, [40] 105 ± 2°, [80] 105–110°, [10,11,39,42,81,82] 110–115°, [83] 110–120°, [84] or 120°C [85], distilling off the water azeotropically with an organic solvent [86], or evacuating in the presence of a drying agent [20,45,52,87-94].

Cation exchangers having a polystyrene–divinylbenzene matrix can be dehydrated without danger of destruction by any of the above methods, but the most convenient treatment in practice is to heat in an air thermostat at 110–115°C to constant weight. The less thermostable sulphophenol–formaldehyde and sulphostyrene–butadiene (SBS resin) cation-exchange resins are appreciably desulphonated under these conditions: it is advisable to dry them over phosphorus pentoxide or magnesium perchlorate at a residual pressure of 5–10 mmHg in a vacuum desiccator.

The equilibrium moisture content of an exchanger is measured by the moisture capacity, expressed as the number of grams or millimoles of water retained by 1 g of the resin or 1 mg-equiv. of functional groups in the state of maximum swelling [87,94]. Determined under rigorously standardised conditions, this quantity is of great value for indicating changes in structure of the matrix on heat-treatment, although it must be accepted with the same reservations as the concept of an "absolutely dry" exchanger. The most reliable method for determining the moisture capacity is to remove adherent water from the fully swollen exchanger by centrifuging [45,94-98] (or by squeezing between sheets of filter paper in the case of membranes [99]), and then dehydrating.

The moisture capacity is closely connected with one of the most important characteristics of exchangers—the relative swellability—that govern their mechanical, kinetic, and catalytic properties. The relative swellability is defined as the percentage increase in volume of the resin in the hydrated state with respect to the volume of the dry resin. Most known methods give only apparent values of this quantity. In particular, the simplest method, involving measuring the volume of the anhydrous and the swollen resin in a cylinder [37,40,100] or in a calibrated column [96], gives values which depend on the granularity of the exchanger. Methods based on measurement of the volume [101,102] or the weight [103] of bound solvent yield in effect the moisture capacity, owing to the breakdown of additivity [94]. The true value of the relative swellability can be determined by measuring the specific volumes [94] or from the increase in volume of a pyknometric liquid in a microburette on the introduction of weighed portions of the resin [41]. Quite reliable values of the relative swellability can be obtained by measuring individual resin particles photographically [104], microscopically [96,105,106], or pyknometrically [40,94,107]. A simple pyknometric method [108]

makes it possible to determine simultaneously density, relative swellability, and moisture capacity, which are interrelated functionally. An interesting method has been described[109] for determining the true density of ion-exchange materials in binary solvent mixtures.

The change in the rate constant for the racemisation of (+)-α-isobutyldeoxybenzoin has recently been used[110] as an indication of the thermal stability of the resin Amberlite-15 when heated in inert media. This approach embodies the idea of a close connection between thermal stability and catalytic activity in ion-exchange materials, which has been expressed repeatedly by the Reviewers in a series of publications.

Since direct methods for recording changes in the structure of exchanger macromolecules have not been discussed in the literature, indirect methods (moisture capacity, relative swellability, sorption properties, etc.) are used. The spectrophotometric method gives interesting details of the chemical structure of a resin macromolecule[77,111-116]. Nuclear magnetic resonance[117-120], electron spin resonance[121,122], and the Mössbauer effect[123,124] are undoubtedly of interest for studying the internal structure, in particular the bonding of water in the resin macromolecule. These methods should find wide application for investigating the thermal stability of exchangers. The application of diverse methods for investigating the properties of exchangers in organic media and in the gas phase[112,125] will provide valuable information on the mechanism of the changes which occur.

The complete characterisation of ion-exchange membranes requires also a knowledge of the changes in selectivity[126-130], electrical conductivity[127,131-136], water permeability[128,131,137], mechanical strength, and specific elongation under tension[138]. It must be remarked that publications very seldom give a complete description of the properties of membranes (or of ion-exchange resins), and this lessens the value of the published results. Authors usually determine only the most important electrochemical properties of membranes, such as the conductivity and the selectivity: a more complete description of the physicochemical properties of membranes will be found in only a few papers[127,128,131].

3. THERMAL STABILITY OF CATION-EXCHANGE RESINS IN GASES AND VAPOURS

The systematic study of the thermal stability of exchangers in air was initiated by the work of Saldadze[139,140]. Using a thermographic method, he observed an endothermic change, probably corresponding to dehydration and occurring in the range 100–130°C depending on the nature of the exchanger. Further heating to 400°C was not accompanied by thermal effects which could be recorded, and this was interpreted[139] as evidence of great thermal stability in the exchangers. Somewhat later Evlanov and his coworkers[141] employed chemical and thermographic methods of analysis to show the presence, on the thermogram of the cation-exchange resin KU-1, of a second endothermic effect at 260–270°C, which was ascribed to the detachment of sulpho-groups. Nevertheless, the titrimetric method employed[141], which gave the total exchange capacity (including phenolic hydroxyls), was insufficiently sensitive to detect small losses of sulpho-groups, and led to the erroneous conclusion that the exchanger had high thermal stability at the temperature of the first endothermic effect (105–115°C). For the same reason no change in concentration of sulpho-groups was noticed[139] at 150°C, and the exchange capacity was judged to be constant from the potentiometric titration curve before and after the heat-treatment of sulphonated phenol–formaldehyde cation-exchange resins. By the use of more delicate methods, involving measurement of the exchange capacity with respect to sulpho-groups alone[8,142] or the loss thereof using the acidity of aqueous extracts, Vasil'ev[8], Polyanskii[142-145], and Jacubovic[20] showed that these exchangers underwent desulphonation at 100°C.

The sulphonated copolymer of styrene and divinylbenzene (KU-2 resin) was considerably more heat-resistant, its exchange capacity remaining unchanged even after 2 months' storage in sealed ampoules at 70°C.[139] When the temperature was raised to 150°C, however, losses in capacity of up to 3% were detected analytically after only 1 day[142].

The loss in weight by the sulphonated cation-exchange resins KU-1 and KU-2 at 110°C is due to the removal of water. The only other substance liberated is sulphuric acid, always in equimolecular proportion to the decrease in exchange capacity at sulpho-groups, independently of the duration of heating[88]. Hence under these conditions desulphonation is due to thermal hydrolysis

$$RSO_3H + H_2O \rightleftharpoons RH + H_2SO_4 \qquad (1)$$

involving residual water in the exchanger. The sulphuric acid which accumulates in the resin absorbs some water from the air, and therefore the weight of the cation exchanger passes through a minimum with continued heating[146].

Raising the temperature to 150° and 185°C leads to the accumulation not only of sulphuric but also of sulphurous acid, their total quantity being molecularly equivalent to the losses in capacity at sulpho-groups, and the proportion of sulphurous acid increases with increased duration of the experiment (in a closed ampoule)[147]. The formation of sulphurous acid is explained by redox reactions of the type

$$Red + H_2SO_4 \rightleftharpoons Ox + H_2O + SO_2, \qquad (2)$$

where Red represents a molecule or an atomic grouping having reducing properties and present in the exchanger[61,148-151], and Ox the corresponding oxidised form.

One of the Reviewers has shown[146,147] that the particle-size distribution of different cation-exchange resins has little effect on the relative losses in exchange capacity. Hence thermal desulphonation can be regarded, not as a topochemical process taking place at the surface of the solid phase in contact with air, but as a chemical reaction occurring throughout the exchanger grain.

The structure of the hydrocarbon skeleton of the matrix, the position of the sulpho-group, and the presence of other substituents in the aromatic ring greatly influence the relative loss of exchange capacity. The maximum thermal stability of the cation-exchange resin KU-2 may be due to an especially stable matrix[1,148], which has a saturated hydrocarbon chain structure. The cation-exchange resin SBS, although an addition polymer, exhibits far lower thermal stability, probably owing to the presence of unsaturated bonds in its matrix. At 185°C its stability is comparable with that of sulphophenol–formaldehyde resins[146]. The latter resins, containing phenolic hydroxyls in the aromatic ring, are unstable even at low temperatures (110°C), their rate of desulphonation increasing with the exchange capacity[143]. On comparing the relative losses in capacity[143] of the cation exchangers KU-1 and Wofatit P, we cannot agree with Naumann's statement[152]

that resins containing sulpho-groups in the side-chain should be more stable. The sulphonaphthalene–formaldehyde resin KU-5, which is monofunctional, is more stable when heated in air than is the cation-exchange resin KU-1G, which has a similar exchange capacity, but is considerably inferior to the resin KU-2.

Decreasing the residual water content in cation exchangers (by raising the temperature of the preliminary drying) slows down the thermal hydrolysis (1). Thus specimens of KU-2 which had been dried at 110° and 130°C lost 37.7% and 17.5% respectively of their exchange capacity after being heated in sealed ampoules at 185°C for 24 h.[146] When heated in open weighing bottles at 185°C for 24 h the exchanger KU-2 loses only 14.5% of its exchange capacity. The reason for these differences in rate of desulphonation is that, when experiments are conducted in sealed ampoules, not only the residual water but also the water formed in the redox reaction (2) takes part in the hydrolysis. The rate of the redox reaction is determined by the structure of the macromolecule and decreases in the sequence KU-1 > SBS > KU-2. Thus in experiments with the cation-exchange resin KU-1 in sealed ampoules at 195°C the proportions of the sulphuric acid formed by hydrolysis that take part in reaction (2) after 1, 6, and 24 h are respectively 46%, 90%, and 100%, but in experiments with KU-2 only 5%, 12%, and 31% respectively[147].

Heating a cation exchanger based on phenoxyethanesulphonic acid and formaldehyde in air for 8 h at 100°, 120°, 130°, 140°, and 150°C produces a change in exchange capacity[153] from 4.30 to 4.40, 4.35, 4.10, 3.80, and 3.75 mg-equiv. g^{-1}. Sulphuric acid is detected in aqueous extracts obtained after the resin has been heated at 130° and 140°C. Oligomers pass into the aqueous extract when the experimental temperature is raised to 150°C.

Thus the quantity of sulphur dioxide evolved cannot be the sole criterion of the thermal stability of a resin. It is not fortuitous that the sequence of thermal stability of sulphonated cation exchangers according to Griesbach[154] varies with the temperature: at 150°C Amberlite IR-100 < Wofatit KS < Wofatit P < Dowex 50 < polynaphthalenesulphonic exchanger = Amberlite IR-120 = Wofatit KPS-20; at 200°C Wofatit P < Amberlite IR-100 < polynaphthalenesulphonic exchanger < Wofatit KS < Dowex 50 < Wofatit KPS 200 < Amberlite IR-120. The thermal stability of the benzylsilane exchanger[154], which is desulphonated above 300°C, is especially noteworthy.

A kinetic interpretation of the experimental results is undoubtedly made difficult by the complicated effect of the redox reaction (2) on the thermal hydrolysis (1). In spite of the large quantity of data which have accumulated on the thermal stability of ion-exchange resins, only the first steps have so far been made in examining the kinetics of the decrease in exchange capacity.

During the initial period of heating in open weighing bottles all the cation exchangers investigated show fairly high rates of desulphonation[144,145,155] (see Table 1), after which the process slows down. Application of first-order and second-order kinetic equations did not reveal a law describing desulphonation for all heating times[145]. This may be a consequence not only of variation in the water content of the resin[146], which should ultimately become constant for a given temperature and relative atmospheric humidity, but also of the presence of energetically non-equivalent sulpho-groups in the exchangers.

Observations[156,157] on the effect of heat-treatment in air on the selectivity and the kinetic properties of sulphonated cation exchangers, which is especially marked in the resin KU-1, are of undoubted theoretical and practical interest. In the absence of heat-treatment, KU-1 absorbs potassium, magnesium, and quinine cations quantitatively from solutions of their salts until breakthrough occurs. Both cations are absorbed from binary mixtures of a solution of quinine sulphate with a salt of one of the above elements in variable quantities. After KU-1 has been heated in air at 150°C, however, none of the organic cations nor magnesium is absorbed from mixtures of potassium or magnesium with quinine, salsoline, or ephedrine, whereas potassium is extracted quantitatively from a comparatively large volume of the filtering solution. Since formation of magnesium complexes of the alkaloids is excluded (absorption proceeds normally on the resin KU-1 before heat-treatment), the observed effect is explained by blocking of the surface of the grain by the large organic cations and loss by the sorbent of the capacity for the bulk absorption of strongly hydrated multivalent ions. In the case of the cation-exchange resin KU-2 preliminary heat-treatment in air at 150° and 185°C is apparent only in a slowing down of ion exchange[156–158] and is accompanied by an increase in the exchange volume capacity.

Table 1. Kinetics of the variation in exchange capacity of cation exchangers in open weighing bottles at 185°C.[144,145,155]

Duration, h	Exchange capacity after heat-treatment, mg-equiv. g^{-1} original resin			Relative loss in capacity, %		
	KU-1	KU-2	KU-5	KU-1	KU-2	KU-5
0	2.01	4.75	3.37	0	0	0
1	1.75	4.64	3.00	12.9	2.8	11.0
3	1.66	4.52	2.72	17.4	4.8	19.3
6	1.35	4.42	2.46	32.9	7.0	27.0
12	1.30	4.26	2.26	35.4	10.3	33.0
24	1.18	4.06	1.98	41.2	14.5	41.3
144	0.59	3.00	1.44	70.7	36.8	57.4
312	0.58	2.40	1.27	71.2	49.3	62.4

The change in the kinetic properties of sulphonated cation-exchange resins and their assumption of the properties of ionic sieves, as a result of heat-treatment in air, can reasonably be attributed to contraction of the three-dimensional structure of the macromolecule. This is supported by the decrease in the equivalent moisture capacity[88,143,156,158].

Treatment of KU-2 with superheated steam produces a decrease in exchange capacity and an increase in the selectivity of the Ag^+–H^+ exchange, which is also explained by structural changes in the resin[159]. Heat-treatment of the sulphonated cation-exchanger SBS in a current of superheated steam at 200°C leads to a slowing down of the van der Waals sorption of phenol, nitrobenzoic acid, and other organic compounds[160], doubtless because of the change in the structure of the sorbent.

The mechanism of the contraction of the three-dimensional network has not been finally elucidated, but it is obvious that preliminary heat-treatment in air may become a method for controlling the kinetic properties of ion-exchange materials.

Heat-treatment of sulphonated cation-exchange resins in air is accompanied also by changes in the relative swellability and in the density in dry and swollen states[155,158].

A possible cause of the decrease in the sorption capacity of sulphonated cation exchangers might have been the formation of weakly acidic groups[55]. However, no new groups of this type are formed in KU-1 and KU-2 on heat-treatment at temperatures up to 185°C.[146] This may be evidence of the insignificant part played up to 200°C by oxidative degradation of the macromolecule. Oxidative degradation of the polymer matrix occurs vigorously at around 400°C and is accompanied by the accumulation of carboxy-groups[161].

The application of the modern methods of thermographic, differential thermographic, thermal, and differential thermal analysis to the investigation of ion-exchange resins has undoubtedly given interesting results[161-165]. With sulphonated cation-exchange resins the last of these methods has revealed[161-163] three endothermic changes, at 100–210°, 270–310°, and above 430°C, which were attributed respectively to dehydration, desulphonation, and oxidative degradation of the matrix. An exothermic effect at 370°C is ascribed to depolymerisation of the copolymer[161]. The elementary composition of the exchangers after heat-treatment is assumed[161,162,164] to indicate partial conversion of sulpho-groups into sulphones and the formation of additional cross-links. Among possible modes of formation of sulphones Soldatov et al.[162] assume direct reaction between sulpho-groups and the matrix:

$$RSO_3H + RH = RSO_2R + H_2O. \qquad (3)$$

At 430°C almost all the sulphur in the resin is already in an inactive state (as sulphones)[161]. Further rise in temperature[161,165] produces intense degradation of the macromolecule with breakdown of the sulphones and formation of sulphur dioxide as the chief sulphur-containing product. Ehlers et al.[165] assume the evolution of this gas to be a consequence of the reaction

$$RSO_2R \rightarrow R\dot{S}O_2 + \dot{R} \rightarrow SO_2 + R{-}R \qquad (4)$$

which occurs by a radical mechanism.

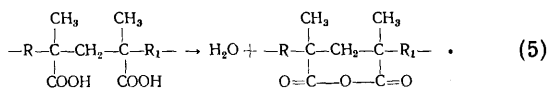
Examination of a single property may lead to erroneous conclusions concerning the behaviour of an exchanger when heated. Thus the existence of two forms of bond between water and functional groups in carboxylated and sulphonated cation-exchange resins (KB-4P and KU-2) was assumed[166] from the number of endothermic effects (at 100–110° and 150–180°C), but this conclusion has not been confirmed by later workers[161-163]. There is also insufficient basis for the conclusion, reached from the results of elementary analysis, that the hydrogen form of the exchanger KU-2, dried at 200°C, contains $1\frac{1}{2}$ molecule of water for every sulpho-group[163]. In view of the partial conversion of sulpho-groups into sulphones[161,162], elementary analysis must be supplemented in this case by alkalimetric titration in order to determine the content of mobile hydrogen ions.

Dependence of the form of thermogravimetric and differential thermal analysis curves on the water content of the original exchanger[162] emphasises the importance of using resins in the same initial state of hydration. The resin dried at 100°C to constant weight, and containing one water molecule for every sulpho-group, may serve as such a state[77].

Desulphonation of the cation exchanger SBR-4 when heated in a current of superheated steam at 200–250°C is accompanied by the formation of volatile products (sulphur dioxide, hydrogen sulphide) and additional cross-links of sulphonyl character with a corresponding contraction of the three-dimensional network and diminution of the moisture capacity[164]. Unfortunately, this interesting investigation[164] was conducted on a non-standard exchanger, which makes it impossible to compare the thermal stability in air with that in superheated steam.

The conversion of sulphonated cation-exchange resins from the hydrogen form into a salt form is accompanied by a significant improvement in their thermal stability in air[140,161,164,167-169]. However, investigation of the behaviour of salt forms of sulphonated cation exchangers is only in its initial stages, and the mechanism of the reactions involved is still obscure.

The behaviour of carboxylated cation exchangers when heated in air has been studied in far less detail than that of sulphonated exchangers, while phosphoric-acid resins have remained almost uninvestigated. From the results of thermographic and chemical examination, together with an analysis of the infrared spectrum, Peryshkina et al.[170] have established that the carboxylated cation-exchange resin KB-4 is stable in the hydrogen form to prolonged heating at up to 120°C. At 200°C the resin loses only water—initially water of hydration, and then water evolved by the condensation of neighbouring carboxyls in the chain:



(5)

Between 200° and 260°C small amounts of carbon dioxide are evolved together with water, as a consequence of decarboxylation[170]. Similar conclusions were reached by Chapiro et al.[171] in a study of the thermal stability of homogeneous membranes based on carboxy-containing monomers. These workers note[171] that reaction (5) slows down when the membranes are heated in a vacuum. Hence atmospheric oxygen plays a definite part in this reaction. The salt forms of carboxylic cation exchangers are more resistant to heating in air than is the hydrogen form[172], as in the case of sulphonic exchangers. The behaviour of the ammonium form of the cation-exchange resin KB-4 is somewhat unusual, for the thermal stability is intermediate between those of the hydrogen and the salt forms[172]. Myagkoi and Suslina's conclusion[172] concerning the energetic non-equivalence of the water of hydration in the exchanger KB-4, which is based on a study of the equilibrium changes in weight of the resin at 100°, 150°, and 200°C, appears to be unsound. The weight of the resin inevitably becomes constant at each temperature, owing to the establishment of sorption–desorption equilibrium between the exchanger and air, provided that decarboxylation and the formation of anhydrides make no significant contribution to the total weight losses.

4. THERMAL STABILITY OF CATION EXCHANGERS IN WATER AND AQUEOUS SOLUTIONS

One of the first papers on the chromatographic separation of rare-earth elements by high-temperature elution[173] mentions the decomposition of the sulphonated phenol–formaldehyde resin IR-1 above 60°C, and Dickel et al.[174] assume that sulpho-groups split off from cation exchangers even during storage of the resins. Calmon and Kressman consider[168] that resins containing cyclic sulpho-groups cannot be used above 40°C, since they undergo hydrolysis with liberation of sulphuric acid. Osborn[175] does not recommend working with ion-exchange resins at temperatures above 70–80°C. Sulphonated cation-exchange resins whose active groups are linked to the aromatic ring through methylene bridges are less liable to hydrolysis[168],

and can be used above 80–90°C. All the authors note that polycondensed sulphonated cation-exchange resins have the greater thermal stability, as when heated in air. According to Lindsay et al.[176] the polymerised cation exchanger Dowex-50 is stable when heated in water up to 105–115°C.

By heating a sulphonated polystyrene cation exchanger in water at 180–210°C Boyd et al.[177] prepared a series of sorbents differing in exchange capacity, in which the quantity of sulphur present in active groups corresponded precisely to that found by elementary analysis. The equivalent moisture capacity of specimens obtained by partial desulphonation passed through a maximum (corresponding to the loss of 50% of the sulpho-groups), its variation showing loosening of the three-dimensional network. The structural changes in sulphonated cation exchangers resulting from their heat-treatment are clearly confirmed by the differences in the coefficients of self-diffusion of ions[177,178] in desulphonated specimens and in the selectivity of ion exchange[91]. The self-diffusion coefficients of Na^+, Ag^+, Zn^{2+}, Y^{3+}, and La^{3+} first increase with decrease in the exchange capacity, pass through a maximum, and then decrease[178]. The equivalent moisture capacity shows a similar variation.

Table 2. Variation in exchange capacity of sulphonated cation-exchange resins when heated in water[146].

Type of exchanger	Temp., °C	Exchange capacity (mg-equiv. g^{-1} initial resin) after heating for			Relative loss in capacity (%) after heating for	
		0	6 h	24 h	6 h	24 h
KU-1	110	2.01	1.84	1.72	8.5	14.4
KU-1	175	2.01	0.17	0.08	91.5	96.1
KU-5	175	1.99	1.77	1.50	11.0	24.6
SBS-3	175	0.91	0.57	0.48	36.7	47.6
KU-2 × 1.5	170	0.87	0.86	0.81	1.3	6.6
KU-2 × 5	170	2.00	1.81	1.61	10.3	19.4
KU-2 × 20	170	1.51	1.21	1.08	19.7	28.3
KU-23 × 3	170	1.17	1.15	1.10	2.0	6.1
KU-23 × 6	170	1.56	1.52	1.47	2.0	5.5
KU-23 × 15	170	1.35	1.25	1.15	7.2	14.9
KU-23 × 20	170	1.40	1.11	0.88	20.6	37.0
KU-2 × 12PS	170	1.87	1.71	1.46	8.8	22.0

The most thorough studies of the thermal stability of sulphonated cation-exchange resins in water have been reported in Refs. 48, 87, 179, and 180. Table 2 gives as illustration the exchange capacity and the relative loss in capacity of specimens when heated in water. The exchange capacity of KU-1 is based on the dehydrated material; in other cases it refers to the state of limiting swelling. The exchange capacity of all the sulphonated resins decreases with rise in temperature and increased duration of heating in water. Owing to the presence of a permanent excess of water, the rate of decrease in the exchange capacity varies more slowly with the duration of heating than in experiments in air. With the same heating time, therefore, the relative loss of exchange capacity is greater in water with some exchangers, and greater in air with others.

Certain conclusions concerning thermal hydrolysis as a cause of the desulphonation of cation-exchange resins in water can be drawn from a comparison of the absolute losses of exchange capacity with the sulphuric-acid content of the aqueous extracts. If thermal hydrolysis is not complicated by redox processes involving the sulphuric acid formed or by the detachment of oligomers containing sulpho-groups, the content of H^+ and SO_4^{2-} ions is double (in number of milliequivalents) the absolute losses of capacity by the exchangers. Table 3 shows that such a correlation has been established, within the limits of experimental error, for the cation exchangers KU-1, KU-2 × 4, and KU-2 × 12PS. In individual cases, e.g. in experiments with KU-5, KU-23 × 15, and especially SBS-3, agreement between losses of capacity calculated from titration of the resin and of aqueous extracts breaks down[146] (Table 3), which may be due not only to redox processes leading to the formation of sulphur dioxide (KU-1 and KU-2) or hydrogen sulphide (SBS) but also to the separation of sulphonic acids of low molecular weight[146,179].

Table 3. Relative loss of exchange capacity after heating for 24 h from titration of resin and of aqueous extracts[146].

Type of exchanger	Temp., °C	Relative loss of capacity (%) from titration of		
		resin	H^+ in extract	SO_4^{2-} in extract
KU-1	175	96.4	95.8	98.5
KU-2 × 4	175	19.5	18.2	19.8
KU-5	175	24.6	23.6	22.2
SBS-3	170	47.6	37.3	—
KU-23 × 15	170	14.8	17.4	17.1
KU-2 × 12PS	170	22.5	23.1	22.3

Table 2 shows that the thermal stability of the sulphonated cation-exchange resins in water diminishes in the sequence—KU-23 × 15 > KU-2 > KU-5 > SBS > KU-1—as in air. In this sequence the condensation polymers KU-32–KU-40 based on aromatic fused-ring systems (anthracene, phenanthrene, pyrene), and the addition polymer KU-3A based on 1-vinylnaphthalene, are probably intermediate in thermal stability[181] between the resins SBS and KU-1. The relative losses of capacity by the exchangers in water depend substantially on the type of exchanger, the chemical structure of its macromolecule, the porosity of the grain (which usually improves stability), and the purity of the initial monomers. Replacement of technical divinylbenzene by the pure *meta*- and *para*-isomers produces some improvement in the stability of the resin, presumably owing to the greater regularity of structure of the macromolecule[182]. Infrared spectroscopy has shown that sulphonation involves partial entry of sulpho-groups into *m*-divinylbenzene[182]. The relative losses of capacity increase with increased quantity of cross-linking agent in gel-like[43] and macroporous[179] samples of the cation exchangers. This rule has been explained hitherto[43,179] by the diminished strength of bonding of sulpho-groups with the matrix due to the increased mutual repulsion between ions as the swelling of the polymer decreases. However, an alternative is to regard the hydrolysis of sulphonated cation-exchange resins as a process catalysed by the hydrogen ions of the sulpho-groups and of the sulphuric acid which is formed. Such a view has been developed in connection with sulphonic acids of low molecular weight[183]. Increase in the degree of cross-linking leads to a decrease in the water content in the exchanger phase, an increased concentration of hydrogen ions relative to water in the vicinity of sulpho-groups, and a consequent increase in the rate of hydrolysis. No direct

connection between degree of cross-linking and the water content of the resin phase exists in macroporous cation exchangers[179]. Their water must be regarded as bound (forming part of hydrate sheaths) and free (filling the pores). Whereas in the desulphonation of gel-like cation-exchange resins[146] the equivalent moisture capacity varies insignificantly, in macroporous specimens it increases continually[179], since the content of free water remains practically unchanged with decrease in the exchange capacity. Moreover, the volume of bound water probably decreases with increase in the content of cross-linking agent even in macroporous exchangers, so that the hydrogen-ion concentration near functional groups and the rate of hydrolysis of the latter also increase.

Many attempts have been made at a kinetic interpretation of experimental results on the hydrolysis of sulphonated cation-exchange resins when heated in water[87,91,146,179,184], but none of them can be regarded as successful, since regularities concerned individual types of exchangers and a limited time interval. Thus a linear relation was found[87] between the logarithms of the loss of capacity and of the duration of heating for the exchangers KU-1 and KU-2, but this rule is by no means always followed by the exchanger KU-5[145] and macroporous specimens[179] based on styrene and divinylbenzene. The relative loss of capacity $\Delta E/E_0$ was found[184] to vary linearly with the duration of heating at 40–90°C with extremely low degrees of desulphonation, and from this the incorrect conclusion was drawn that hydrolysis of the sulpho-groups in the cation exchangers KU-1, KU-11, sulphonated coal, Zeocarb-215, Wofatit P, KU-21, KU-5, and KU-6G conforms to a first-order rate law.

The logarithm of the mean rate of desulphonation of the cation exchanger Dowex-50 × 12 was shown[91] to vary linearly with the reciprocal of the absolute temperature, which indicated that the hydrolysis of sulphonated cation-exchange resins obeys the Arrhenius equation.

In none of the above investigations was the formation of weakly acidic groups detected when sulphonated cation-exchange resins were heated in water. Therefore the conclusions[185] that such groups appear when the sodium form of the cation exchanger Ankalit KT-3 is heated in water at 90–100°C for 100 h, and that some of the sulpho-groups are converted into sulphonyl groups, are somewhat unexpected. In our opinion the basis for these conclusions is insufficient.

Heating sulphonated cation exchangers in water is accompanied not only by a decrease in exchange capacity but also by changes in swelling and moisture capacity. The increase in the swelling of KU-1 and KU-2 as a result of being heated in water at 100°C is accompanied by an increase in their electrical conductivity[186].

Boyd et al.[177] attribute the slight increase in the equivalent moisture capacity of gel-like cation exchangers to a decrease in the number of cross-links in the matrix on heating in water. However, it was shown later[87] that the changes in equivalent moisture capacity are reversible, and level out after drying followed by swelling in water.

The same effects occur when heat-treated KU-2 and KU-1 are regenerated with alkali and acid with complete (KU-2) or partial (KU-1) restoration of the electrical conductivity[186]. In view of the reversible character of the changes in moisture capacity on heat-treatment, one of the Reviewers has attributed them to temporary deformation of the three-dimensional network under the influence of immobilised water[87].

Heating macroporous cation exchangers in water produces a redistribution of pore size, while the total porosity remains unchanged[179]. This observation opens up methods for controlling the properties of ion-exchange materials.

The salt forms of cation exchangers[168] (KU-1[87], MSF[140], polystyrenesulphonate[177], polycyclohexadiene[187]) show considerably better thermal stability than the hydrogen form when heated in water, as in air. At 175°C appreciable desulphonation effects are observed only with KU-1 resin[87]. The thermal stability of sulphonated cation-exchange resins depends on the nature of the gegenion, and diminishes in the sequence of ionic forms $Mg^{2+} > Ca^{2+} > Na^{+} \gg H^{+}$.[180] Thus when KU-1 was heated in these ionic forms at 150°C for 1 day, the corresponding losses in exchange capacity were 21.6%, 25.2%, 29.6%, and 81.2%.[180] The rule found for the series of salt forms can reasonably be explained by desulphonation by the reaction[87,180]

$$RSO_3M + H_2O = RH + MHSO_4 . \quad (6)$$

The hydrogen ions liberated by the hydrolysis (6) undergo ion exchange

$$RSO_3M + MHSO_4 = RSO_3H + M_2SO_4 \quad (7)$$

replacing some of the metal ions in the sulpho-groups and lowering the thermal stability of the exchangers.

The abnormally low thermal stability of the hydrogen form of KU-1 in comparison with other cationic forms was explained by hydration of the hydrogen ion in the resin and by its special polarisation and quantum-mechanical properties[180]. However, if hydrolysis of the sulpho-groups is considered in terms of acid catalysis, the above experimental results find an unequivocal explanation. In fact, heating KU-1 under conditions excluding access of hydrogen ions to the resin phase (in a carbonate buffer)[188] does not result in desulphonation at 150°C. From the above discussion, it is easy to understand why the sodium form is less stable than the magnesium and calcium forms: in conformity with the charge and radius of the hydrated ion, sodium is most easily replaced by the hydrogen ion in the resin phase. However, the magnesium form is more stable than the calcium form, although according to the exchange constants the magnesium ion should be replaced more easily by the hydrogen ion in the resin phase. This apparent discrepancy is eliminated by assuming that the equilibrium

$$(RSO_3)_2Ca + H_2SO_4 \rightleftarrows CaSO_4 + 2\,RSO_3H \quad (8)$$

shifts to the right because the calcium ions in the liquid phase are bound as the relatively sparingly soluble sulphate[180]. A more general view may be to assume that the equilibrium is reversed at high temperatures owing to variation in the molar volumes of the hydrated exchangeable ions[189], as follows from the Gregor–Glückauf equation[190].

Thus the thermal stability of the salt form of a resin in an unbuffered medium can be discussed only arbitrarily, with the realisation that actually it is determined by the proportion of sulpho-groups present in the hydrogen form.

The changes in other physicochemical properties (density, swelling, moisture capacity, etc.) which occur when the salt forms of sulphonated cation-exchange resins are heated in water are essentially the same as those observed with the hydrogen form[87,88].

Published assessments of the stability of sulphonated cation-exchange resins in alkaline and acidic media are contradictory. The suggested[148] low resistance of sulphophenol–formaldehyde exchangers to the action of alkalis is partly confirmed by experiment. Thus the exchange capacity of Wofatit P is diminished by prolonged (> 40

min) boiling with 0.1–1.0 *N* potassium hydroxide solutions, but is unaffected by shorter treatment[140]. Another phenolsulphonic exchanger, Dowex 30, loses its exchange capacity when heated in 1 *N* caustic soda above 100°C, but the observed losses are nevertheless smaller than with the hydrogen form of the exchanger under the same conditions. At high pH-values the polymer structure breaks down with separation of an organic compound even at moderate temperatures. Nevertheless, according to Lindsay et al.[178] the properties of the addition polymer Dowex-50 are unaffected by brief heating in solutions of pH 10.5 and in 1 *N* caustic soda up to 168°C. In weakly alkaline media sulphophenol–formaldehyde cation exchangers[191] and the condensation polymers KU-5 and KU-6 are completely stable both in the cold and on heating[78,192]. The decrease in exchange capacity observed in some cases when phenol–formaldehyde cation exchangers are heated in alkaline media[140,148] is probably due, not to hydrolytic elimination of sulpho-groups, but to degradation of the macromolecule and separation of sulphonates of low molecular weight.

Heating in dilute non-oxidising acids also produces larger losses in capacity of sulphonated phenol–formaldehyde resins than of polystyrene resins. A monograph[193] mentioned the possibility of using sulphonated polystyrene cation exchangers in acid media at temperatures up to 120°C. Other results[139] indicate breakdown of sulphonated phenol–formaldehyde resins on prolonged boiling in dilute hydrochloric and sulphuric acid, but no definite conclusions can be drawn owing to the absence of a comparison between the action of these media and that of water. The loss in capacity of KU-1 at 100°C has been found[194] to diminish with increase in the concentration of sulphuric acid, being 92%, 72%, and 48% after 6 h in the 0.1 *N*, 0.5 *N*, and 1.0 *N* acid respectively. This was explained[194] by suppression of hydrolysis of the sulpho-groups in sulphuric-acid media, but this contradicts other conclusions[147].

Homogeneous sulphonated cation-exchange resin membranes based on polyethylene[195] are not very stable in alkaline media. After being kept in 10 *N* potassium hydroxide solution at room temperature their electrical resistance has fallen from 0.51 to 0.26 ohm cm^2.

Membranes based on fluorinated polymers are probably the most promising with regard to thermal stability and chemical resistance. According to Chapiro and Seidler[171] graft membranes based on tetrafluoroethylene and acrylic acid are stable at room temperature in 6 *N* caustic potash, water, and concentrated solutions of hydrochloric acid, sulphuric acid, and potassium carbonate, but undergo decarboxylation and dehydration with conversion of the carboxyls into anhydrides when heated to 200°C. The polytetrafluoroethylene matrix remains unchanged for 140 h at 200°C.

According to Munari and his coworkers[196,197], sulphonated cation-exchange membranes based on styrene grafted to tetrafluoroethylene can function for a long time in water at 180°C (in the hydrogen form) and at 280°C (in the salt forms), but in concentrated solutions of sodium hydroxide, sulphuric, hydrochloric, and nitric acids, and a mixture of hydrochloric and nitric acids at temperatures above 100°C. Unfortunately, these conclusions were not supported by experimental results.

In oxidising acids the hydrolytic elimination of sulpho-groups is accompanied by degradation and oxidation of the matrix. Thus the addition of potassium chromate to dilute sulphuric acid greatly diminishes the stability of the cation exchanger KU-1 owing to simultaneous desulphonation and redox processes[194]. Kazantsev et al.[198,199] showed by means of infrared spectroscopy that the desulphonation of KU-1 in dilute nitric acid is accompanied by the entry of nitro- and carboxy-groups into the aromatic rings of the matrix. Losses of capacity by KU-1 in 3 *N* nitric acid are enormous even in the cold, reaching 50% after 24 h. Under the same conditions KU-2 loses up to 25% of its capacity. The exchanger SDV-3 is completely desulphonated after being heated in the presence of 1 *N* nitric acid at 90°C for 30 days. Investigation by several independent methods of the behaviour of KU-2 at 20° and 80°C in solutions of potassium bromate and dichromate, hydrogen peroxide, and nitric acid indicated[200] fundamental structural changes in the resin and the occurrence of a variety of reactions.

A study[201] of the stability of the sulphonated cation-exchange resins KU-2, KU-2 × 8chs, KU-2P, and KU-22 in 6 *N* sodium hydroxide solution and in 3 *N* nitric acid at 75°C indicated that KU-2 was the most stable with respect to change in weight. However, variation in weight cannot be regarded as an unambiguous criterion of the stability of exchangers. In nitric acid the exchange capacity of the resins even increases. Atroshchenko et al.[202] observed no changes in capacity or signs of breakdown of the macromolecule when KU-2 was regenerated in the cold with 13–26% nitric acid. However, the exchanger broke down with the evolution of oxides of nitrogen when boiled in 40% nitric acid for 2 h. The working exchange capacity of a filter bed of this resin was 5% less than that of a layer which had been subjected to 16 cycles of treatment with 15% nitric acid in the cold and to 19 cycles with 40% nitric acid. After this the capacity of the resin remained unchanged during normal operation[202].

Cation exchangers containing sulpho-groups in the side-chain (Wofatit P, Stacionit F) are more stable in solutions of various oxidising agents (hydrogen peroxide, potassium permanganate, chromic acid) than are resins having sulpho-groups in the ring (KU-1G)[149]. In our opinion the statement that Wofatit P is more stable than the sulphonated polystyrene cation-exchange resin in permanganic acid and hydrogen peroxide containing iron(III) salts[149] requires verification. Additions of tervalent iron and other ions which accelerate the decomposition of hydrogen peroxide greatly intensify the breakdown of the sulphonated polystyrene cation exchanger Permutit Q in 50% hydrogen peroxide at 60°C, with rupture of cross-links and ultimately complete dissolution of the resin[203]. These processes most probably involve the intermediate formation of hydroperoxides, which are converted into sulphonic acids of low molecular weight. According to Wiley and Reich[204] the stability of sulphonated copolymers of styrene with 8% of divinylbenzene in 3% hydrogen peroxide in the presence of iron(II) sulphate at 75°C is strongly dependent on the purity of the monomers and the nature of the divinylbenzene isomer. The rate of desulphonation is highest with the technical cation exchanger Dowex-50 × 8, and decreases in the series of resins containing *p*-divinylbenzene, technical divinylbenzene, and *m*-divinylbenzene. Complete breakdown of the exchangers is observed after 270–300 min.

Raising the temperature accelerates the changes in capacity, density, and especially swelling of the exchanger KU-2 on treatment with oxidising agents[205]. Correct procedures were used in this work[205] to prove the formation of carboxylic, ketonic, and alcoholic groups when the oxidants attacked C–H bonds in methylene groups and at tertiary carbon atoms. Mixtures of nitric acid with potassium bromate and with potassium dichromate possessed greater oxidising power than these oxidants alone,

hydrogen peroxide, or ammonium peroxodisulphate[205]. The sulphonated cation exchanger and membranes based on $\alpha\beta\beta$-trifluorostyrene[206] show no change in properties when heated with 3% hydrogen peroxide in the presence of Fe^{3+} ions at 70°C for 24 h. Under these conditions the loss in weight of a phenol–formaldehyde exchanger is 97%, and those of sulphonated styrene–divinylbenzene cation exchangers containing 1%, 2%, 4%, 8%, and 12% of divinylbenzene are respectively 62%, 46%, 26%, 11%, and 6%. The great stability of the new exchanger towards oxidants was explained[206] by the greater strength of the C–F bond than of the C–H bonds (103 and 77 kcal $mole^{-1}$).

Many authors assign great importance to elementary oxygen as a sensitiser of the aging of resins[58,84,140,207] by the rupture of cross-links. Industrial establishments, therefore, undertake the deaeration of water or add reducing agents (e.g. sodium sulphite), in this way increasing the useful life of the exchangers to many years[207]. It must be remarked, however, that the important question of the role of oxygen in determining the thermal stability of ion-exchange resins has not yet found due recognition in laboratory investigations, and needs to be studied systematically.

Very little study has been made of the stability of phosphoric-acid cation exchangers towards thermal hydrolysis[208,209]. Published information enables only a few general conclusions to be drawn: with the same structure of hydrocarbon network in the macromolecule the phosphoric-acid exchangers (KF-1, KF-11,[209] and SF [208]) are more stable than the sulphonated exchangers (KU-2), but the stability also falls with increase in the divinylbenzene content. The difference in behaviour between salt forms and the hydrogen form is far smaller than with the sulphonated exchangers[208]. In contrast to the latter, porous specimens of phosphoric-acid resins possess lower thermal stability than the gel-like resins[209]. Changes in exchange capacity after heating in water are larger at the less thermostable strongly acidic groups than at the weakly acidic groups[209]. However, this interpretation cannot be accepted, since the exchangers investigated contained $-PO(OH)_2$ groups, which dissociate in two stages. In our opinion the observed effects are more plausibly explained by variation in the proton-donor power of the active groups resulting from heat-treatment of the exchangers.

5. THERMAL STABILITY OF SULPHONATED CATION-EXCHANGE RESINS IN ORGANIC MEDIA

The use of sulphonated cation-exchange resins as catalysts in various organic syntheses[35] stimulated interest in the study of their behaviour in organic media. Before the appearance of experimental results it seemed to many authors[210,211] that such exchangers should exhibit great thermal stability in organic media. Thus Astle[211] was sure that they could be used in organic media up to 180°C, but expected rapid breakdown under more severe conditions. Saldadze et al.[210] consider that they can be used in hydrocarbon media at 150–170°C.

However, the very first experimental results showed that assumptions of great thermal stability were too optimistic. Thus Andreas[212] used a sulphonated phenol–formaldehyde exchanger as catalyst for the esterification of acetic acid by ethanol and by butanol, and of adipic acid by methanol, and found that the resin was not wholly stable to heating above 120°C. He observed that Wofatit P decomposed with the evolution of sulphur dioxide and formaldehyde at temperatures above 180°C. Losev and Trostyanskaya[213], who used the exchangers MSF and SBS as catalysts for the preparation of butyl butyrate, found that the catalytic activity and the acidity (a measure of exchange capacity) of both resins fell rapidly with increased number of cycles. In view of the poor stability of the exchangers, these workers[213] recommend that they should not be employed above 120°C.

According to Menyailo et al.[214] the exchangers KU-2 and SBS show poor stability when used to catalyse the hydration of propene at 160–170°C. Naumann[152] found the polycondensation exchangers Wofatits P and F to be inferior in stability to the polyaddition resin Wofatit KRS-200. Solubility data indicate that all the resins are more stable in non-polar than in polar solvents.

Systematic investigation of the behaviour of sulphonated cation-exchange resins in various organic media was begun by the present Reviewers[42,47,112,215–217].

The relative losses of exchange capacity found by titrating the resin and the aqueous extracts (R_k and R_a), which are compared in Table 4, indicate that KU-1 is less stable than KU-2 in hydrocarbon media, as when heated in water and in air. The losses in exchange capacity by KU-1 are almost the same in hydrocarbons and in air[215,217]. The thermal stability of KU-2 resin, on the other hand, is lower in hydrocarbon media[42,216,217]. At 100°C, however, the effects of different media even out[42,215].

Table 4. Relative losses in capacity (%) of cation-exchange resins after being heated in various media.

Expt. No.	Temp., °C	Duration, h	Air		Isopentane		Isopentenes		Ref.
			R_k	R_a	R_k	R_a	R_k	R_a	
KU-1 cation exchanger									
1	100	10	11.3	10.9	—	—	12.8	10.9	215
2		120	24.6	23.7	—	—	26.0	23.7	
3		240	25.6	25.1	—	—	30.3	24.1	
4	125	10	17.5	18.5	—	—	14.7	15.2	
5		120	31.4	22.6	34.0	—	37.8	23.5	
6		240	39.7	29.4	42.0	—	43.7	34.3	
KU-2 cation exchanger									
7	150	10	6.7	6.5	5.7	4.6	7.8	4.8	46
8		24	6.6	6.5	7.7	5.6	13.1	5.0	
9		120	10.1	8.5	11.0	5.4	37.0	3.4	
10	200	2	12.0	9.7	15.0	7.5	36.0	5.4	
11		10	26	12	41	5.4	65	1.7	
12		24	54	15	62	6.1	75	2.6	

The diminished stability of KU-2 in alkenes[42,216,217] is explained by a weakening of the R–SO_3H bond as a consequence of the formation of a carbonium ion from the alkene and the hydrogen ion of the sulpho-group[215], and also by redox reactions the products of which (H_2O) either take part in or promote thermal hydrolysis. Formation of carbonium ions and redox interaction are less marked with saturated than with unsaturated hydrocarbons, and therefore KU-2 resin is more stable in the former. However, KU-2 is less stable in isopentane[42,216] and benzene[217] than in straight-chain alkanes and in air. Benzene and alkanes containing a tertiary carbon atom probably form π-complexes and carbonium ions with the gegenions of the active groups[218]; they undergo redox interaction with sulphuric acid.

The lack of effect of the medium on the thermal stability of the exchanger KU-1, like the low rate of polymerisation of alkenes in its presence, is explained[215] by steric hindrance to the formation of carbonium ions. It is interesting that the catalytic activity of KU-1 in the polymerisation of alkenes is enhanced by grinding or by pretreatment with methanol in a Soxhlet extractor[219]. However, the activation of the exchanger is only temporary, and disappears after heating at 150°C for a short time[219].

Comparison of the values of R_k and R_a (Table 4) shows that the nature of the medium affects the course of the redox reactions. Identical values of R_a and R_k indicate the transfer of sulpho-groups to degradation products as sulphuric acid owing to hydrolysis (1) involving the residual water in the exchanger. With rise in temperature and increase in duration of heating, sulphuric acid accumulates in the reaction products until it reaches a concentration at which redox reactions involving molecules of the resin and of the medium can occur. The reducing properties are, of course, more pronounced for alkenes than with alkanes[42,216,217]. Reducing activity increases in the series of resins—KU-2, KU-1, SBS.[220]

An empirical linear relation[42] $\lg E = f(\lg \tau)$ describes the kinetics of the variation in the exchange capacity of KU-2 in air, isopentane, and isopentenes, as in water. The slope of the straight line serves as a qualitative indication of the effect of the medium on the rate of desulphonation. The temperature dependence of the loss of capacity in KU-2 obeys the Arrhenius equation[217].

The breaks between the linear portions of the $\lg E - \lg \tau$ graphs probably indicate acceleration of hydrolysis of the sulpho-groups in the exchangers by the redox reaction (2) and its products. The correctness of such an interpretation is supported by the agreement between the abscissa for the break and the start of the redox reactions[42].

The rate of desulphonation is unaffected by the grain-size of the exchanger KU-2, contamination with traces of sulphonic acids of low molecular weight, or the relative proportion of resin and isopentenes[47]. This confirms the fact established previously, that the desulphonation of cation-exchange resins is controlled by an actual chemical reaction (hydrolysis) occurring throughout the resin[146,147].

Increasing the divinylbenzene content from 3% to 7% does not affect the thermal stability of the cation exchanger KU-2, but further increase in the degree of cross-linking (to 17% of divinylbenzene) is accompanied by a decrease in thermal stability. It is interesting that the ratio of the losses in capacity by a strongly and by a weakly cross-linked specimen of the exchanger decreases with rise in temperature and increase in duration of heating. Thus when resins containing 17% and 7% of divinylbenzene are heat-treated for 10, 24, and 48 h the ratio $R_k^{(17)}/R_k^{(7)}$ is respectively 1.94, 1.52, and 0.91.[47] Similar relations have been established in the heat-treatment in water of KU-2 containing 24% and 12% of divinylbenzene[43] for which the ratio of the losses in capacity $R_k^{(24)}/R_k^{(12)}$ after heating at 150°C for 6, 24, and 120 h is respectively 1.94, 1.69, and 1.25. This levelling of the rate of elimination of sulpho-groups from specimens having different contents of divinylbenzene was explained[47] by an equalisation of the electrostatic interaction between functional groups. However, such an explanation is equivocal. An alternative view relates the change in thermal stability to the existence of energetically non-equivalent sulpho-groups, the number of which should increase with increase in the degree of cross-linking in the resin. When the resin is heated in any medium, weakly bound sulpho-groups (e.g. those occupying the *ortho*-position in styrene-2,4-disulphonic acid) should be the first to split off; but when equivalent sulpho-groups remain (occupying the *para*-position), the effect of the degree of cross-linking should level out.

A comparative study of the behaviour of various cation exchangers when heated in air and in isopentenes showed that, as in aqueous media, the thermal stability increased in the sequence KU-1G < KU-1 < SBS < KU-2[146,220]. Addition polymers in the above series are more stable when heated than are polycondensation exchangers. Experiments with KU-1 and KU-2 revealed that polymerisation of the alkenes inevitably led to acceleration of the loss of exchange capacity. Different results were obtained with the resins SBS and KU-1G: the polymerisation of isopentenes is catalysed by SBS, although its thermal stability is the same in air and in isopentenes; yet KU-1G is almost without catalytic effect on this reaction, although its thermal stability in isopentenes is less than in air. This anomaly has not yet been explained satisfactorily, and requires further study.

A detailed chemical, potentiometric, and spectrophotometric (infrared) investigation of the cation exchanger KU-2 established[112] that, under all conditions of heat-treatment in air up to 200°C, all the sulphur is present in sulpho-groups. When KU-2 is heated in isopentane, a small portion of the sulphur passes into an "inactive" state. A considerably larger quantity of "inactive" sulphur is present after the resin has been heated in isopentenes. Successive treatment of the resin with alkali and acid converts part of the "inactive" sulphur into a state which is active with respect to ion exchange, and is included in the determination of sulpho-groups. This "inactive" sulphur is assumed[112] to be present as *S*-esters of thiosulpho-groups $R.SO_2.SR'$, where R and R′ are organic radicals of the resin and of a thiol. The infrared spectra show that severe heat-treatment of KU-2 in air and in isopentane can cause sulpho-groups to migrate from the *para*- to the *meta*-position, and polyphenyl bonds may be formed, with a decrease in the equivalent moisture capacity[112].

Table 5. Effect of content of water in KU-2 resin on its thermal stability at 150°C.[216]

Expt. No.	Water in resin, %	Relative loss in exchange capacity, %							
		in air after				in isopentenes after			
		1 day		2 days		1 day		2 days	
		R_k	R_a	R_k	R_a	R_k	R_a	R_k	R_a
1	*	2.4	1.8	2.8	2.0	4.0	2.4	7.1	2.4
2	**	6.6	6.5	7.5	8.2	13.1	5.0	25.8	2.8
3	24.2	12.2	14.0	18.0	19.5	8.6	6.6	14.4	6.2
4	48.4	9.6	9.2	10.0	10.0	9.6	8.2	9.0	11.2
5	57.3	6.2	6.8	8.2	9.0	4.8	6.8	8.6	8.8

* Exchanger dehydrated at 150°C
** At 110°C.

Bound water is involved in the hydrolysis of sulphonated cation exchangers, and has a great influence on the occurrence of reactions (1) and (2)[216] (Table 5). With increased water content the relative loss in capacity passes through a maximum, whose position and height depend on the nature of the medium. In air the maximum losses of capacity occur in a resin containing 24% of water.

The increase in the rate of hydrolysis of sulpho-groups as the water content of the resin increases to 24% is probably due, not only to the autocatalytic action of the sulphuric acid[216], but also to the easier transport of H_3O^+ ions to the hydrolysable C–S bond. Further increase in the water content of the resin inevitably dilutes the sulphuric acid in the exchanger phase and diminishes its catalytic activity.

In contact with isopentenes the losses in capacity are largest with a specimen of the resin which has been dehydrated at 110°C. Developing the earlier views[216] we must suggest that direct reduction of sulpho-groups by the alkenes with the formation of sulphur-containing compounds is probable, as is redox interaction between sulphuric acid and reducing groups in the resin or the medium. According to Table 5 use of a resin which has been dehydrated at 150°C is most favourable for the occurrence of such processes.

If the choice of catalyst for organic synthesis is guided solely by considerations of thermal stability, well dehydrated exchangers are to be preferred. However, the removal of water may hinder dissociation of the active groups, and thereby have an adverse effect on the catalytic activity of the exchanger. The resin KU-2 in a state of limiting swelling at 150°C catalyses the isomerisation of 3-methylbut-1-ene into 2-methylbut-2-ene and 2-methylbut-1-ene[121], the hydration of isopentenes to t-pentyl alcohol, and the polymerisation of alkenes[216]. In the presence of an exchanger containing up to 24% of water no hydration of isopentenes occurs, only polymerisation. The inability of hydrate water in KU-2 of moisture content 24.2% (or 3.5 mmoles H_2O mg-equiv.$^{-1}$ sulpho-groups) to effect hydration is probably due to its very strong bonding to the sulpho-groups. This is supported by data[222] indicating that absorption of the first three molecules of water on each sulpho-group in the resin is accompanied by a large heat release. The exchanger KU-2 which has been dehydrated at 110°C exhibits the maximum catalytic activity for the polymerisation of isopentenes: further dehydration at 150° and 175°C lowers the activity[216].

The infrared spectra show that catalysis yields sulphur-containing compounds and small amounts of aromatic compounds—degradation products of the polymeric matrix—as well as polymers. Chemical, potentiometric, and polarographic analyses have established the presence of elementary sulphur, thiols, and alkyl sulphides among the products of catalysis[112]. The difference between the total sulphur content found by elementary analysis and the aggregate quantity present as the above compounds was attributed to polysulphides and sulphoxides[112].

Sulphur dioxide and hydrogen sulphide were detected in the gas phase[125]. With experiments in isopentane and in air, the gas phase contained only sulphur dioxide, but the aqueous extracts contained both sulphuric and sulphurous acids[125].

The whole range of reactions which occur when the cation-exchange resin KU-2 is heated in hydrocarbons[112,146], discussed above, can be summarised as indicated below.

Resin Phase

The fall in the exchange capacity is governed by hydrolysis of sulpho-groups involving residual water (reaction 1). This is accompanied by redox interaction of the resulting sulphuric acid with reducing groups of the macromolecule (reaction 2). In media which undergo no chemical reactions, the changes undergone by cation exchangers are confined to these two reactions. In alkenes sulphones may be formed:

$$RSO_3H + C_5H_{10} = RSO_2{-}C_5H_9 + H_2O \qquad (9)$$

and also *S*-esters of thiosulphonic acids:

$$RSO_3H + C_5H_9SH = RSO_2{-}SC_5H_9 + H_2O. \qquad (10)$$

It is quite probable that sulphuric acid may take part in the formation of polyphenyl cross-links:

$$-CH_2-\underset{|}{CH}-C_6H_5 + -CH_2-\underset{|}{CH}-C_6H_5 + H_2SO_4 = 2H_2O + SO_2 + \\ + -CH_2\underset{|}{CH}-C_6H_4-\underset{\diagdown\,CH_2}{\overset{/}{C}}-C_6H_5 \,. \qquad (11)$$

Liquid Phase

The following changes are possible in the liquid phase.

1. Processes involving isopentenes and catalysed by hydrogen ions from the resin: (*a*) isomerisation of alkenes[112,221]

$$CH_3-\underset{|}{CH}-CH=CH_2 \xrightarrow{H^+} \begin{cases} \rightarrow CH_3-\overset{CH_3}{\overset{|}{C}}=CH-CH_3 \\ \rightarrow CH_2=\overset{CH_3}{\overset{|}{C}}-CH_2-CH_3 \end{cases} \qquad (12)$$

(*b*) polymerisation of isopentenes

$$n\,C_5H_{10} \xrightarrow{H^+} (C_5H_{10})_n \qquad (13)$$

(*c*) hydration of isopentenes

$$C_5H_{10} + H_2O \xrightarrow{H^+} C_5H_{11}OH \,. \qquad (14)$$

2. Reactions between alkenes and desulphonation products: (*a*) formation of sulphonates

$$C_5H_{10} + H_2SO_4 \rightarrow C_5H_{11}{-}OSO_3H \qquad (15)$$

$$2\,C_5H_{10} + H_2SO_4 \rightarrow C_5H_{11}{-}OSO_2O{-}C_5H_{11} + 2\,H_2O \qquad (16)$$

(*b*) formation of sulphoxides[223]

$$2\,C_5H_{10} + SO_2 \rightarrow C_5H_9{-}SO{-}C_5H_9 + H_2O \qquad (17)$$

(*c*) formation of thiols

$$C_5H_{10} + H_2S \rightarrow C_5H_{11}SH \qquad (18)$$

(*d*) formation of polysulphides

$$x\,C_5H_{10} + y\,S \rightarrow (C_5H_{10})_xS_y \,. \qquad (19)$$

The sulphur consumed in reaction (19) has been formed by the interaction of sulphur dioxide and hydrogen sulphide: $2H_2S + SO_2 \rightarrow 3S + 2H_2O$.

3. Reactions of derivatives of alkenes: (*a*) disproportionation of sulphoxides into sulphones and sulphides

$$2\,C_5H_9{-}SO{-}C_5H_9 \xrightarrow{H^+} C_5H_9{-}S{-}C_5H_9 + C_5H_9{-}SO_2{-}C_5H_9 \qquad (20)$$

(*b*) formation of aldehydes and thiols from sulphoxides

$$C_5H_9{-}SO{-}C_5H_9 \xrightarrow{H_2O} C_5H_9SH + C_4H_7C\overset{O}{\diagdown\!\!\diagup H} \qquad (21)$$

(*c*) formation of dialkyl disulphides in the presence of atmospheric oxygen

$$4\,C_5H_9SH + O_2 \rightarrow 2\,C_5H_9{-}S{-}S{-}C_5H_9 + 2\,H_2O \qquad (22)$$

(*d*) reaction between dialkyl disulphides and water

$$C_5H_9{-}S{-}S{-}C_5H_9 + H_2O \rightarrow C_5H_9SH + C_4H_7C\overset{O}{\diagdown\!\!\diagup H} + H_2S \qquad (23)$$

(*e*) formation of sulphides

$$C_5H_{11}SH + C_5H_{10} \rightarrow C_5H_{11}{-}S{-}C_5H_{11} \,. \qquad (24)$$

This whole complicated system of changes, including catalytic reactions, has a decisive effect on the thermal stability of the cation exchanger KU-2 in tertiary pentenes and determines the composition of the products.

The existence of a connection between the thermal stability of cation exchangers and catalytic reactions of the medium is confirmed by analogous investigations of resins in alcohols[217,224], phenol[225], and acetone[225]. Table 6 shows that the thermal stability of the cation exchangers KU-1 and KU-2 depends on the nature of the alcohol. Losses in capacity by KU-2 increase, whereas those of KU-1 decrease, as the alcohol molecules become larger. At 150°C the exchanger KU-1 is almost completely desulphonated after 24 h. At 125°C losses in capacity by KU-1 are almost the same in ethanol, n-pentanol, and isopentanol, but considerably greater than in t-pentyl alcohol or decanol. At 100°C the effect of the nature of the alcohol on the thermal stability of KU-1 levels off, and the losses in capacity after 24 and 120 h in ethanol are 16.6% and 36%, compared with 12.2% and 38.8% in decanol[224].

Table 6. Thermal stability of sulphonated cation-exchange resins in alcohols[217,224].

Temp., °C	Duration, h	Loss in capacity of resin, %									
		ethanol		n-pentanol		isopentanol		t-pentyl alcohol		decanol	
		R_k	R_a	R_k	R_a	R_k	R_a	R_k	R_a	R_k	R_a
KU-1 cation exchanger											
125	24	55.2	22.5	62.2	18.7	59.3	15.3	43.1	38.8	26.8	22.5
150	24	92.9	73.5	100	80.4	96.5	69.5	96.1	70.0	39.2	20.0
KU-2 cation exchanger											
150	10	3.0	2.6	7.1	5.5	3.6	5.0	7.4	6.6	10.0	4.8
	24	7.0	5.8	12.0	12.0	9.4	8.6	12.4	11.4	15.6	6.2
	48	8.2	6.8	15.2	11.6	17.2	13.2	14.4	12.2	18.5	1.6

The discrepancy observed between R_k and R_a cannot be explained by redox reactions of type (2), since alcohols are dehydrated to ethers and alkenes

$$2\,C_5H_{11}OH \xrightarrow{H^+} C_5H_{11}OC_5H_{11} + H_2O \quad (25)$$

$$C_5H_{11}O{-}C_5H_{11} \xrightarrow{H^+} 2\,C_5H_{10} + H_2O \quad (26)$$

in the presence of sulphonated cation exchangers[35], and the water that is formed dilutes the sulphuric acid, whose redox potential is lowered. Since no sulphur-containing compounds were present in the gas phase, the discrepancy was explained by the assumed formation of esters of the alcohols with sulphuric acid and with sulpho-groups of the resin[217,224]

$$C_5H_{11}OH + H_2SO_4 \xrightarrow{H^+} C_5H_{11}{-}O{-}SO_3H + H_2O \quad (27)$$

$$C_5H_{11}OH + RSO_3H \rightarrow RSO_2O{-}C_5H_{11} + H_2O\,. \quad (28)$$

As the alcohol molecules become larger, the relative solvation of the KU-2 falls, and the corresponding increase in concentration of active groups accelerates esterification[224]. These factors tend to accelerate the thermal hydrolysis of cation exchangers in alcohols in comparison with the rate of this process in water[224].

Examination of the thermal stability of KU-2 in phenol and in acetone[225] reveals an apparent breakdown in the usual type of relation between catalytic reactions of the medium and the stability of cation-exchange resins. In the presence of KU-2 phenol does not undergo any chemical change other than oxidation by air. Acetone gives various condensation products and water even in the cold. It would appear that KU-2 should be less thermostable in acetone than in phenol. However, experiment indicates that the thermal stability of the resin decreases on passing from acetone to its mixtures with phenol and to phenol itself[225]. This "anomaly" is explained by formation of a large quantity of water on the condensation of acetone; this water is sorbed by the resin and tends to increase its thermal stability[216].

The condensation products of acetone accumulate in the "pores" of the exchanger, shield the sulpho-groups, and may lead to a loss of catalytic activity by the resin even in the absence of thermal hydrolysis. The process of shielding must be distinguished from blocking of the sulpho-groups by their direct interaction with molecules of the medium to form such compounds as esters (with alcohols).

Thus the investigations give an idea of the specific character of the processes occurring in exchanger macromolecules in organic media. First, a correlation between thermal stability and catalytic activity is clearly revealed in cation exchangers. Secondly, the thermal hydrolysis of cation exchangers in organic media is not the only cause of the diminution in exchange capacity, for its competes with blocking and screening of the ion-exchange groups. Thirdly, the relative loss of capacity in organic media is determined by the composition and the properties of the reaction system as a whole (including reaction products), not only by the added liquid reagent. Unfortunately, the question of the effect on thermal stability of the distribution of components between liquid phase and resin has not yet been raised.

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Experimental results which have accumulated show that the main reason for the decrease in exchange capacity of ion-exchange materials when heated and subjected to corrosive media is the detachment of functional groups, in most cases by hydrolysis. Among the numerous factors influencing the strength of bonding between active groups and the matrix, and therefore the thermal hydrolysis of the exchangers, the nature of the heat-treatment medium, the chemical structure of the exchanger macromolecule, and the nature of the functional group and its gegenion are especially important.

The medium in which the exchanger is heated affects the decrease in exchange capacity in four cases: (1) the medium or its reaction products interact with the functional groups; (2) the medium undergoes catalytic reactions involving the gegenion of the functional group (polymerisation of hydrocarbons, esterification of alcohols, condensation of ketones, etc.); (3) the molecules of the medium form unstable addition products, including π-complexes, with the functional groups; or (4) the "pores" of the resin grains are filled with reaction products of the medium that shield the functional groups (products of the condensation of acetone, the polymerisation of alkenes, etc.). Hence it follows that the necessity of considering the thermal stability and the catalytic activity of ion-exchange materials together with their reactions is dictated not only by the requirements of a right choice of catalysts but also by considerations of the causal relation between these properties in molecular terms.

Some interesting relations between the chemical structure and the thermal stability of the exchangers have been revealed. As in the lower sulphonic acids, the electron-donor phenolic hydroxyls in sulphonated phenol–formaldehyde cation exchangers facilitate electrophilic substitutions. Therefore all phenolsulphonic acids of high molecular weight undergo hydrolysis more easily than, and are inferior in thermal stability in the media investigated to, sulphonated cation exchangers having a polystyrene–divinylbenzene matrix. The cation exchanger SBS is inferior to KU-2 resin in thermal stability, perhaps because butadiene groups have a stronger polarising action than have divinylbenzene groups on the C–S bond. Increase in the degree of cross-linking of sulphonated polystyrene exchangers is accompanied by an increase in the rate of hydrolysis of the sulpho-groups. Thus variation in the chemical structure of the matrix may be an effective means for the planned synthesis of thermostable cation exchangers.

With matrices of the same structure the liability of cation exchangers to undergo thermal hydrolysis and other processes leading to a change in exchange capacity depends on the nature of the active group. This aspect needs to be studied thoroughly, but it can already be stated that sulphonated exchangers are less stable than resins containing phosphate and carboxylate groups. The hydrogen forms of the exchangers, like the ordinary oxy-acids, are less stable than the corresponding salts. On the other hand, it must be emphasised that very few investigations have been made on the thermal stability of the salt forms, despite their importance; this gap must be filled in the near future.

However, the main task in investigating the thermal and chemical stability of ion-exchange materials is, in our opinion, to study the elementary processes occurring in exchangers and leading to deterioration in their operational properties, and also to establish the kinetics of these processes. Progress in this field will undoubtedly contribute to the development of methods for the planned synthesis of ion-exchange materials having specified properties and satisfying the demands of modern science and technology.

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While the manuscript has been awaiting publication, several papers have appeared which have deepened our knowledge of the thermal stability of cation-exchange resins. They include detailed thermographic investigations[226-228], and new generalisations on the thermo-oxidative degradation of carboxylated exchangers[229].

Individual papers[230,231] have raised the question of the useful life of cation-exchange resins as catalysts of organic reactions under industrial conditions at 130–150°C. Experience indicates[230] that, after use as an alkylation catalyst for 40–45 days, KU-2 loses its activity and cannot be regenerated. In our view the development of methods for the regeneration of cation exchangers requires the closest attention, and is urgently required for their practical employment in several catalytic reactions conducted at high temperatures.

The work of Paushkin and his pupils[232-235] on the preparation of thermostable cation exchangers containing a system of aromatic rings in the conjugated chain is worthy of special mention. However, a direct study of thermal stability in various media is required to assess the prospects for new cation exchangers.

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Thorough Elimination of Acetylenic Hydrocarbon Impurities from Various Mixtures

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Acetylenic hydrocarbons are a very undesirable impurity in many instances of polymerisation, oxidation, and other syntheses. The problem of the elimination of acetylene derivatives from various mixtures has been investigated in fair detail: patent data are particularly numerous. This review is based on studies published up to 1970; an attempt has been made to give a systematic account of and to compare the advantages and disadvantages of various methods and procedures for the thorough elimination of the above impurities and certain physical properties of the principal components of the mixtures purified and analytical methods for the determination of the acetylenic hydrocarbon impurities have been examined.
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I. INTRODUCTION

One of the particularly undesirable impurities, which are difficult to remove and which have a significant influence on the polymerisation of monomers and the quality of polymers[1-8], cause explosions in oxygen works[9], and inhibit the oxidation of organic compounds, are acetylenic hydrocarbons (AH). Therefore, the increase in the manufacture of large-scale products of the petrochemical industry such as ethylene, propene, isobutene, halogenoethylenes, isoprene, butadiene, and others, produced by the pyrolysis and dehydrogenation of hydrocarbon raw materials or synthesised from raw acetylene, must inevitably involve the development of effective processes whereby acetylenic hydrocarbons can be thoroughly removed. In particular the polymer industry imposes very vigorous requirements on the purity of the monomers. Thus ethylene and propene used in high-pressure polymerisation and vinyl chloride must not contain more than 0.0005 vol. % of acetylenic hydrocarbons[10-13] and their content in isoprene and butadiene should not exceed 0.0004 and 0.005 wt. % respectively[14]. In the future the requirements which will have to be met by methods for the elimination of acetylenic hydrocarbon impurities from industrial mixtures and by methods for the analytical control of technological processes will naturally become more stringent.

Many procedures have been described for the thorough elimination of acetylenic hydrocarbon impurities from hydrocarbon and non-hydrocarbon mixtures involving various methods. However, so far no review has been published on this practically important problem. In the present review the procedures and methods for the thorough elimination of acetylenic hydrocarbon impurities from various mixtures are described and critically assessed from the standpoint of their suitability in practice.

II. SOME PHYSICAL PROPERTIES OF THE MAIN COMPONENTS OF THE MIXTURES PURIFIED[15-25]

The Table lists certain physical properties of the main components of the mixtures purified and also mixtures of the acetylenic hydrocarbon impurities.

III. METHODS FOR THE THOROUGH ELIMINATION OF ACETYLENIC HYDROCARBON IMPURITIES FROM VARIOUS MIXTURES

The following methods are known for the removal of acetylenic hydrocarbon impurities from various gaseous and liquid mixtures: sorption, distillation, catalytic hydrogenation, catalytic oxidation, catalytic polymerisation, and certain others.

1. SORPTION

The sorption purification methods are based on the enhanced absorption capacity of certain sorbents—liquids, salt solutions, and solid porous materials—in relation to acetylenic hydrocarbons. Therefore three technological processes are usually employed for the purification:
(a) absorption by liquids; (b) adsorption by solids;
(c) chemical interaction between the acetylenic hydrocarbon and the sorbent, i.e. chemisorption.

a. Absorption by Liquids

Acetylenic hydrocarbons and in particular acetylene (A) are comparatively readily soluble in many organic solvents[26-28], in contrast to many other hydrocarbon and non-hydrocarbon compounds. This property of acetylenic

Some physical properties of the principal components of mixtures from which the acetylenic hydrocarbon impurity is removed.

Substance	Mol. wt, M	M.p., °C	B.p., °C (760 mmHg)	Specific gravity relative to air (0°C, 760 mmHg)	Specific gravity of liquid d_4^{20}, g cm^{-3}	Refractive index n_D^{20}	Cryst. temp., °C	Crit. pressure p, atm	Explosion limits in mixtures with air, vol.%	Heat of combustion, Q_{comb}, kcal mole^{-1}	Thermal conductivity, 10^5 cal cm^{-1} s^{-1} deg^{-1}
Hydrogen	2.016	—259.20	—252.78	0.0695	0.0763$^{-253.3}$	—	—239.9	12.8	4.0—74.2	68.77	41.60
Nitrogen	28,016	—210.02	—195.81	0.9673	0.8622$^{-208.4}$	—	—147.1	33.5	—	—	5.80
Oxygen	32.00	—218.83	—182.97	1.1053	1.2489^{-205}	—	—118.8	49.7	—	—	5.89
Carbon monoxide	28.01	—205	—191.5	0.9669	0.8471^{-205}	—	—140.2	34.5	12.5—74.2	68.32	5.14
Methane	16.04	—182.44	—161.58	0.5545	0.3242^{-107}	1.00044°	— 82.1	45.8	5.0—15.0	212.79	7.02
Acetylene	26.04	—80.8^{1277}	— 83.8	0.9073	0.6154$^{-80.3}$	0.00051	35.3	61.6	2.5—80.0	311.36	4.40
Ethylene	28.05	—169.19	—103.7	0.9749	0.5699$^{-103.4}$	1.363^{-100}	9.7	50.9	2.7—28.6	337.28	3.92
Ethane	30.07	—182.81	— 88.63	1.0488	0.5612^{-100}	1.00075°	32.27	48.2	3 2—12.5	372.8	4.31
Methylacetylene	40.06	—104.7	— 23.23	—	0.690 $^{-40}$	—	128	52.8	—	465.1	—
Propene	42.08	—185.25	— 47.75	1.4804	0.6095^{-47}	1.3567^{-40}	91.8	45.6	2.0—11.1	491.82	3.33
Propane	44.09	—187.65	— 42.06	1.554	0.5794^{-40}	1.3395$^{-42.5}$	96.81	42.01	2.4—95.0	530.57	3.59
Diacetylene	50.06	— 36.4	10.3	—	0.7364°	—	—	—	—	—	—
Vinylacetylene	52.08	—138	5	—	0.6876	—	168	50.7	—	—	—
Butadiene	54.09	—108.92	— 4.47	1.8832	0.650°	1.4292^{-25}	152	42.7	2.0—11.5	618.1	—
Dimethylacetylene	54.09	— 32.3	26.97	1.918	0.6906	1.3893^{25}	215.5	—	—	—	—
Ethylacetylene	54.09	—125.72	8.07	—	0.6906	—	190.5	—	—	—	—
Isobutene	56.10	—140.35	— 7.01	1.9336	0.6268$^{-6.6}$	1.3796^{-25}	144.73	39.48	—	647.2	3.08
α-butene	56.10	—185.3	— 6.25	1.9336	0.6182°	1.3777^{-25}	146 4	39.7	1.7— 9.0	649.66	3.08
cis-β-butene	56.10	—138.9	3.72	—	0.6213	1.3932^{-25}	157	41	—	—	2.48
trans-β-butene	56.10	—105.5	0.88	—	0.6042	1.3842^{-25}	157	41	—	—	2.85
butane	58.12	—138.35	— 0.50	2.091	0.5789	1.3600^{-25}	152	37.5	1.8— 8.4	687.94	3.22
Isobutane	58.12	—159.4	— 11.72	2.067	0.5572	1.3503^{-25}	134.9	36.0	1.8— 8.4	686.3	3.12
Propylacetylene	68.12	—106.1	40.23	—	0.6940	1.4079^{18}	—	—	—	—	—
Isopropylacetylene	68.12	—	29.0	—	0.6854°	1.3756	—	—	—	—	—
Ethylmethylacetylene	68.12	—109.3	56.12	—	0.7127^{17}	1.4004	—	—	—	—	—
Isoprene	68.12	—145.95	34.067	2.358	0.6809	1.4216	—	—	1.7—11.5	—	—
α-pentene	70.14	—165.2	29.97	—	0.6405	1.3715	201	40	—	803.4	—
cis-β-pentene	70.14	—151.37	36.94	—	0.6555	1.3828	202.4	40.4	—	—	—
trans-β-pentene	70.14	—140.2	36.35	—	0.6482	1.3793	202.4	40.4	—	—	—
α-isopentene	70.14	—168.5	20.06	2.428	0.648	1.3640	191.4	33.9	—	807.63	—
β-isopentene	70.14	—133.78	38.57	2.428	0.6623	1.3869	191.6	35.3	—	795.7	3.12
pentane	72.14	—129.7	36.08	2.4872	0.6259	1.3576	196.6	33.3	1.4—78	845.27	3.12
Isopentane	72.14	—159.89	27.85	2.4872	0.6197	1.3539	187.8	32.9	1.3—	843.36	2.91
Vinyl fluoride	46.04	—160.5	— 72.2	—	0.853 $^{-72.2}$	—	54.7	53.35	—	—	—
Vinyl chloride	62.49	—159.7	— 13.9	—	0.9730^{-15}	1.38^{-15}	150.4	55	3.65—26.6	17.59	—
1,1-Difluoroethane	66.05	—	— 24.7	—	—	—	113.5	44.4	—	—	—
1,1-Dichloroethane	98.95	— 96.7	57.3	—	1.174	1.4166	—	—	—	—	—
1,2-Dichloroethane	98.95	— 35.5	83.5	—	1.253	1.4448	—	—	6.2—16	—	—

hydrocarbons is used to extract them from a wide variety of complex systems in order to free them from this impurity.

A number of procedures have been developed and proposed for the removal of acetylene from coking gas[29-31], cracking gas[32-34], and gases involved in the partial oxidation[35] and high-temperature pyrolysis[36] of hydrocarbons, which contain it in an amount of 7—10 vol. %. Acetylacetone, methanol, kerosene, acetone, dimethylformamide (DMF), *N*-methylpyrrolidinone, ethyl methyl ketone, butyrolactone, and others are employed as selective solvents. The absorption process is usually carried out in several stages, mainly at temperatures between −30° and −70°C and pressures in the range 10—16 atm. The degree of extraction of acetylene is not more than 97—99%.

Many studies have been made on the develoment of a process for the preparation of ethylene free from the acetylene impurities using selective absorption of the latter. The majority of investigators[32-47] suggest that acetylene be selectively extracted from the crude ethylene or the C_2 fraction obtained from the coking and cracking gases or the gases from the pyrolysis of the hydrocarbon raw material. Acetylene is absorbed from the C_2 fraction by selective solvents at a temperature close to the liquefaction temperature of the mixture and at an elevated temperature. However, ethylene containing about $1-10^{-4}$ vol. % of acetylene, compared with its initial concentration in the mixture of 0.05—1.58 vol. %, could be obtained in only a few cases[43,44,46].

The method of selective absorption by organic solvents is used to eliminate acetylene from halogenated hydrocarbon mixtures. Thus treatment of vinyl chloride containing 0.18 vol. % of acetylene with methanol in a countercurrent absorber yields a product containing only 0.006 vol. % of acetylene[48]. Insignificant amounts of acetylene are removed from its chlorination products by passing the hydrocarbons mixed with a solvent (water, acetone, etc.) continuously through an injector or an ejector[49]. Dimethylformamide, dimethyl sulphoxide, *N*-methylpyrrolidinone or their mixtures have been proposed as selective solvents[50-54] for the separation of gaseous mixtures consisting of 67—85 vol. % of vinyl fluoride, 15—31.5 vol. % of acetylene, and admixtures of other hydrocarbons. However, the vinyl fluoride concentrate isolated contained about 0.8 vol. % of acetylene.

When isoprene containing 1.4 mole % of higher acetylene hydrocarbons is treated with an aqueous solution of dimethylformamide at 0°C, the amount of impurity diminishes only to 1.0 mole %.[55] In addition, many absorption procedures for the extraction of acetylene from various gases evolved in the processing of hydrocarbon raw materials with the aim of concentrating it have been described, but these will not be considered here.

b. Adsorption by Solids

The adsorption of acetylene on artificial zeolites of type 4A and 5A, activated charcoal of type KST, and silica gel of type MSM from gases produced in the oxidation of methane by air and oxygen at temperatures between −78° and +80°C has been investigated[56]. According to the results, zeolites show promise in the extraction of acetylene from gases produced by the incomplete oxidation of methane and in the thorough removal of acetylene from industrial gases, for example ethylene.

A process has been developed for the adsorption elimination of traces of acetylene from air in apparatus employing gaseous and liquid oxygen by means of zeolites of types NaA and CaA.[57-59] A high efficiency of purification is achieved at 20–70°C and when the acetylene content in the initial mixture is not more than 2.4 $cm^3\ m^{-3}$. When the average content of acetylene in air is 0.03 $cm^3\ m^{-3}$, one ton of type CaA zeolites purify without regeneration $9 \times 10^6\ m^3$ of air and operate for 300 h. However, CaA zeolites have a high regeneration temperature (350°C) and, when the concentration of acetylene in air is about 1 $cm^3\ m^{-3}$, their dynamic activity falls sharply. The adsorption properties of various ion-exchange forms of type A and X zeolites with various degrees of substitution of sodium by the cations of other metals have been investigated[60]. It has been found that the optimal form is a type X zeolite with a low degree of substitution of sodium by transition-metal cations. Together with a high adsorption capacity in relation to acetylene (15.8 cm^3 of acetylene per 100 cm^3 of zeolite), it has a low regeneration temperature (250° to 300°C). Other investigators[61] recommend KSM silica gel as an adsorbent for the same purpose. At temperatures between −100° and −160°C, it absorbs acetylene from the gas stream almost completely. KSM silica gel has been recognised as the best agent for the purification of the ethylene fraction obtained in the low-temperature separation of coking gas[62]. At a gas space velocity of 840 h^{-1} and a temperature of −100°C and below, it absorbs acetylene to the extent of 30–80% and its homologues to the extent of 80–95%. Treatment of liquid ethylene in an autoclave under a pressure of 19 atm at −30°C in the presence of an adsorbent comprising a mixture of alumina gel and silica gel[63] makes it possible to reduce the acetylene content in ethylene from 4.4×10^{-3} to 7×10^{-4}%.

The possibility of the employment of continuous adsorption for the removal of acetylene from vinyl chloride[64-66] and for the selective extraction of acetylene from gases produced by the incomplete oxidation of methane[67-71] has been investigated. When Hungarian activated charcoal with a specific surface of 996 $m^2\ g^{-1}$ was employed and the process was carried out at 20°C, a pressure of 1.5 atm, and a space velocity of about 200 h^{-1}, fractions virtually free from acetylene were obtained.

c. Chemisorption

In order to improve the efficiency and selectivity of the processes for the sorption extraction of acetylenic hydrocarbons from various mixtures, the chemisorption principle, i.e. chemical binding of acetylenic hydrocarbons by sorbents, which usually contain copper, silver, or mercury compounds, has been used in a number of cases.

Numerous studies have been made[72-86] on the selective elimination of acetylenic hydrocarbons from the C_4 fractions with a high content of diolefins, for example butadiene, before the extraction of the latter.

Acetylenic hydrocarbons are chemisorbed from such gaseous or liquid fractions by treatment with an aqueous ammonia solution of copper(I) acetate at temperatures between −10° and +10°C. The acetylenic hydrocarbons then form soluble complexes with copper and remain in solution. They are desorbed by heating the solution to 80–105°C, sometimes using a desorbing gas, for example ammonia[83]. On desorption, part of the artylenic hydrocarbons are polymerised; the high-molecular-weight compounds are separated by passing the solution through a layer of activated charcoal. The acetylenic hydrocarbon impurity (0.15–0.3 wt. %) can be extracted by this procedure only to the extent of 70–95%. It has been stated[80] that, under the purification conditions, butadiene is sorbed by the solution 150 times less effectively than acetylenic hydrocarbons. In order to remove small amounts of acetylenic hydrocarbons from gaseous mixtures, the hydrocarbons are chemisorbed by an ammoniacal solution of copper(I) chloride with formation of copper acetylide precipitates. In particular, the use of this solution for the thorough elimination of the acetylene impurity from vinyl fluoride[8,87] results in an acetylene content in the purified gas not greater than 4×10^{-5} vol. %. With this method of purification, the content of higher acetylenic hydrocarbons in alkenes diminishes from 0.3 to 0.001 wt. %.[88] Acetylenic hydrocarbons are removed from streams of ethylene and butadiene by passing them through a solution of copper(I) chloride in dimethyl sulphoxide[89]. It has been noted that the copper acetylides formed under these conditions are less explosive and more stable than those known hitherto. Thorough removal of acetylenic hydrocarbons from hydrocarbon fractions containing butadiene or isoprene is achieved by rapidly passing the gaseous mixtures at 50° to 100°C through a suspension of metallic sodium in xylene[90-92]. The acetylenic hydrocarbons are then completely extracted: acetylene is bound as the acetylide and the higher acetylenic hydrocarbons are polymerised.

Procedures have been described[93-95] for the removal of acetylene from gaseous mixtures containing it in amounts of 14–29 vol. % by passing them through a suspension of VB or VIB metal halides or complexes in aliphatic or naphthene hydrocarbons. The degree of extraction of acetylene is 76–96%. A method for the elimination of acetylene from crude ethylene by treating a stream of ethylene with an aqueous solution of a mercury(II) salt in the presence of oxygen and iron(III) ions has been patented[96]. Such treatment for 1 h results in a decrease of the concentration of acetylene in ethylene from 0.67 to 0.003 vol. %.

Chemisorption by solids is used to eliminate acetylenic hydrocarbons from gas streams, for example from ethylene. Zeolites based on silver[97] and also silver halides and copper(I) and mercury(I) halides or oxides dispersed on porous carriers (alumina gel, silica gel, etc.) have been proposed as sorbents[98,99]. A high efficiency of purification is achieved only when the amount of the acetylenic hydrocarbon impurity in the streams undergoing purification is very low. For example, when the process is carried out using a type X zeolite containing about 35 wt. % of silver at 65°C and a space velocity of 18 000 h^{-1}, ethylene containing 2×10^{-5} vol. % of acetylene is obtained when the initial acetylene concentration is 6×10^{-4} vol. %.

The sorption methods for the removal of acetylenic hydrocarbon impurities are frequently employed on a semi-industrial or industrial scale[32,34,36-39,41,42,57-61,67-71,73,86]. However, in most cases[32,34,44,53,62,63,77,83,84] they do not reduce the acetylenic hydrocarbon content in the mixtures purified to the required limit. For many hydrocarbon systems the selectivity of the sorption method is low, as a result of which a considerable amount of the main products (up to 10%) is lost together with the acetylenic hydrocarbons removed. The industrial employment of the chemisorption procedures involves serious difficulties. The process becomes explosive, since explosive copper acetylides are always formed[100]. The spent solutions are not satisfactorily regenerated[101], which leads to a non-productive consumption of copper salts. Therefore the chemisorption method is largely used in analytical chemistry for the detection and quantitative determination of very low

concentrations of acetylenic hydrocarbons, in particular acetylene, in gaseous mixtures[102-120]. Moreover, the sorption procedures for the removal of acetylenic hydrocarbons involve a considerable consumption of reagents, are complicated, and laborious. Nevertheless, in large-scale manufactures, the absorption of acetylenic hydrocarbons by selective solvents at a low temperature under high pressure is an effective method for the preliminary separation of comparatively large amounts of acetylenic hydrocarbons present in various hydrocarbon systems. The subsequent additional thorough elimination of small amounts of acetylenic hydrocarbons can be achieved by other methods.

2. DISTILLATION

The distillation methods are most suitable for the separation of complex hydrocarbon mixtures into individual fractions in terms of the number of carbon atoms. The isolation of individual components from these fractions and even more so the removal of acetylenic hydrocarbons with the same number of carbon atoms involve considerable difficulties and require clear-cut fractionation. Nevertheless the method of low-temperature fractionation is used in some cases to remove acetylenic hydrocarbon impurities from hydrocarbon mixtures.

Procedures have been proposed for the preparation of pure vinyl chloride by fractionating the acetylene hydrochlorination products[121-123] or the products of the interaction of acetylene with 1,2-dichloroethane[124]. The yield of vinyl chloride containing 0.005 mole % and less of acetylene amounted to about 90% on a column equivalent to 30 theoretical plates (t.p.) with a reflux number of 10.

The possibility of the preparation of specially pure vinyl chloride by a fractionation method has been investigated and it has been shown[125] that, in a column with the same efficiency as above but with a reflux number of 23, it is possible to isolate about 90% of vinyl chloride containing less than 0.001 mole % of acetylene and other impurities, except methylacetylene. The removal of the latter requires a column equivalent to more than 60 theoretical plates. Other investigators[126] obtained by this method vinyl chloride containing 5.5×10^{-7} mole % of acetylene.

When the boiling point of the acetylenic hydrocarbons and the main substances are very close, for example in the case of diolefins and higher acetylenic hydrocarbons or vinyl fluoride and acetylene, the usual fractionation method is relatively ineffective and leads to the loss of considerable amounts of the products purified. In such cases extractive[127,128] or azeotropic fractionation[129-133] is employed. A gaseous mixture comprising vinyl fluoride and 1,1-difluoroethane is freed from the acetylene impurity by azeotropic fractionation with ethane, which forms with acetylene an azeotrope boiling at −94.5°C. The product specimens obtained contained 1–5 vol. % of ethane and 0–2 vol. % of acetylene[129,130]. Azeotropic fractionation of mixtures containing butadiene with an admixture of isobutane[131,132] resulted in a decrease of the concentration of vinylacetylene from 0.49 to 0.08 wt. %.[122] It has been suggested that rectified isoprene be freed from the acetylenic hydrocarbon impurity by azeotropic fractionation in the presence of isopentane and maleic anhydride[133]. Columns equivalent to 60–90 theoretical plates are normally employed. With a reflux number of 50, the acetylenic hydrocarbon content in the mixture becomes only several times smaller.

The distillation methods for the removal of acetylenic hydrocarbons are widely used in the industrial manufacture of vinyl chloride and butadiene. The purification processes are carried out on high-efficiency columns with high reflux numbers. Nevertheless they do not ensure a high degree of purification[134] and result in a loss of up to 10% of the desired product even when the difference between the boiling points of the components is considerable[123,125]. A clear-cut low-temperature fractionation is restricted by the risk of explosion of acetylenic hydrocarbons in the liquid and solid states and in the gaseous state under pressure. The extractive and azeotropic fractionation procedures somewhat alleviate the above difficulties but here too the desired products are frequently contaminated by additional impurities[129,130]. Therefore the distillation method can be employed successfully for the preliminary elimination of acetylenic hydrocarbons in the purification of various products with subsequent additional fine purification by more effective methods, for example by hydrogenation[135].

3. CATALYTIC HYDROGENATION

The first studies on the selective hydrogenation of acetylenic hydrocarbons in the presence of olefins were carried out in the USSR.[136,137] It proved possible to reduce even very small amounts of acetylenic hydrocarbons to ethylenic derivatives in the presence of a large excess of the latter. It was shown that the process selectivity depends on the catalysts employed and the hydrogenation conditions.

Palladium dispersed on various carriers (alumina gel, silica gel, activated charcoal, glass, etc.) is widely used as a catalyst for the removal by selective hydrogenation of the admixture of acetylenic hydrocarbons from concentrated olefinic fractions (C_2 and C_3),[11,138-157] butadiene[158-161], coking gas[162-166], and vinyl fluoride[167]. The hydrogenation is usually carried out in the gas phase at 100–320°C, 5–50 atm, and a space velocity up to 20 000 h^{-1} using catalysts containing 0.001–0.1 wt. % Pd. In many cases[143,148,160,166] the amount of acetylenic hydrocarbons in the streams undergoing purification diminishes from 0.8 to $(1-5) \times 10^{-4}$ vol. %. In order to enhance the initial selectivity, the catalyst is first treated with hydrogen at a working pressure and a temperature higher by 30 deg than the working temperature[168,169]. Frequently, in order to ensure a high selectivity of the catalyst in the hydrogenation of acetylenic hydrocarbons, it is promoted with copper, silver, iron[170-175], chromium[176,177], lithium[161,178], ruthenium, and rhodium[179,180], the process is carried out in the presence of water vapour[181], and the mixture undergoing purification is inhibited with alkyl sulphides[182], halogeno-derivatives of aromatic hydrocarbons[183], or cyclohexane derivatives[184].

Catalysts containing platinum are used to eliminate acetylene from ethylene mixtures[185] and coking[186,187] and other industrial gases[188] at an elevated temperature and pressure. The concentration of acetylene in the purified streams is 2×10^{-4} vol. % and less. Methods have been patented in which concentrated C_2 and C_3 fractions are freed from acetylenic hydrocarbons by liquid-phase hydrogenation between −40° and +50°C and at pressures between 12 and 36 atm on palladium, platinum, or mixed nickel–thorium catalysts[189-191]. The content of acetylenic hydrocarbons then falls from 0.7 to 0.002%.

Apart from platinum subgroup metals, other metals and their compounds are also employed as catalysts for the

selective hydrogenation of acetylenic hydrocarbons. In particular, nickel on kieselguhr is used for the liquid-phase hydrogenation of acetylenic hydrocarbons in the butene–butadiene fraction of the gases obtained in the pyrolysis of petroleum products[192,193], in the dehydrogenation products of isopentane and isopentenes, or in concentrated isoprene[194,195]. As a result, acetylenic hydrocarbons are removed to the extent of approximately 75–95%. The elimination of small amounts of acetylenic hydrocarbons from olefins and diolefins is achieved by hydrogenation over catalysts consisting of reduced nickel[196-201], a mixture of nickel[202,203] or cobalt[204] oxides and sulphides, and nickel or cobalt[205] phosphides on a porous carrier. The process is carried out at 20–315° and pressures up to 70 atm; it yields a product containing less than 1×10^{-4} vol. % of acetylenic hydrocarbons. When ethylene containing 7.6 vol. % of acetylene is passed through a catalytic solution of a nickel cyanide complex at 0–60°C, the effluent gas contains only 0.2 vol. % of acetylene[206]. Mixed nickel–chromium catalysts on carriers are used in the purification of cracking gases[207] and in the gases produced in the pyrolysis[208,209] of a hydrocarbon raw material and in the ethylene fraction of coking gas[210] and the crude ethylene–propene fraction[211]. Selective hydrogenation is carried out at 100–400°C, pressures up to 30 atm, and a space velocity in the range 300–6000 h^{-1}. As a result, virtually complete elimination of acetylenic hydrocarbons from the mixtures is achieved. Catalysts consisting of mixtures of the oxides of cobalt and molybdenum[212,213], nickel and molybdenum[214], and cobalt, nickel, and molybdenum or chromium[215-218] or the sulphides of cobalt, nickel, and molybdenum[219,220] on alumina proved to be effective and selective catalysts. In order to improve the selectivity of the hydrogenation process and to increase the useful life of the catalyst, acetylenic hydrocarbons are removed in the presence of water vapour or sulphur compounds[216]. The above catalysts ensure the elimination of acetylenic hydrocarbons from olefins and diolefins to the extent of 92–100%. Iron–chromium and copper–chromium catalysts promoted with alkali and alkaline earth metal compounds are used to eliminate acetylenic hydrocarbons from olefinic and diolefinic hydrocarbons[221-231] and the gases produced in the processing of mazut[232] at 30–370°C, a pressure up to 70 atm, and a space velocity in the range 200–1000 h^{-1}. The purified products contain about 3×10^{-4} vol. % of acetylenic hydrocarbons, while their initial concentration was 0.16 vol. %. It has been noted that iron–chromium catalysts[221-224,232] give rise to a prolonged induction period in the course of which the products underoing purification are consumed. The purification of converter gas on a zinc–chromium–copper catalyst[233], of pyrolysis gases on an aluminium–chromium–nickel catalyst[234], and of ethylene on a copper–chromium–manganese catalyst[235] has been investigated. In many cases these catalysts ensure virtually complete removal of acetylenic hydrocarbons and have considerable advantages over other catalysts tested, for example those containing palladium, platinum, iron, etc. The effective elimination of acetylene from coking gas[236,237] and concentrated olefins[238] is achieved by its selective hydrogenation on silver catalysts at 150–400°C, 11–15 am, and a space velocity of 3000–4000 h^{-1}. The concentration of acetylene in the gases after purification is 0.0003–0.008 vol. % for an initial concentration of 0.15–0.8 vol. %. The acetylenic hydrocarbon impurity is removed from olefins and diolefins by hydrogenation at 38–315°C, pressures up to 70 atm, and a space velocity in the range 100–2500 h^{-1} using copper catalysts[239,240], sometimes promoted with zinc[241] or Group VIII metals[242]. For example, acetylene is hydrogenated to the extent of 97% on a copper–zeolite catalysts[240], the yield of ethylene being 60% and of ethane 40%. Processes for the removal of acetylenic hydrocarbons from butadiene on an iron powder catalyst at somewhat elevated temperatures and pressures[243], from coking gas on a boron oxide catalyst at 300°C, 50 atm, and a space velocity of 2000–10 000 h^{-1},[244] and from olefin-containing mixtures by bringing them into contact with a palladium–molybdenum catalyst at 200–430°C[245] have been described. Three catalysts (their composition has not been published) for the selective hydrogenation of acetylene in gases from the thermal cracking of ethane, propane, and heavy hydrocarbons have been investigated[246]. The catalysts were tested at 177–316°C, 3–10 atm, and a space velocity of 500 h^{-1}. The concentration of residual acetylene in the purified gases did not exceed 1×10^{-4} vol. %.

The method of selective catalytic hydrogenation has been recognised as the most economical among the existing procedures for the removal of acetylenic hydrocarbons from hydrocarbon mixtures[247,248]. It is widely used in industry[11,144,164,166,181,193,208,218,233,246-252] and in most cases ensures the required degree of purification. However, the hydrogenation method frequently requires the use of expensive palladium and platinum catalysts, which are the most selective[253] but are also very sensitive to other impurities[254] and are difficult to regenerate[255,256]. Moreover, in the purification process the desired products are hydrogenated together with the acetylenic hydrocarbons[193-195,200,208,250,257]. The activity of the catalyst employed is particularly high in relation to the hydrogenation of conjugated bonds in diolefins[192,193,195,256,258] and therefore the losses of the latter in purification are considerable, reaching 8–20%.[145,161,193] As a result it proved possible to achieve the simultaneous elimination of acetylenic hydrocarbons and diolefins from mixtures with a high olefin content[149,176,189-191,209,234,259]. In the case of acetylenic hydrocarbons which also contain a double bond, the hydrogenation of the triple bond is not selective[258,260,261]. Many hydrogenation catalysts have a very prolonged (up to several days) induction period during which the desired products are consumed[222-224] and some of them lose their initial selectivity during operation[262] and lead to the occurrence of side reactions with formation of a wide variety of substances[263-265]. Therefore studies are being made in order to find and develop new catalysts and hydrogenation methods. In particular, in the elimination of acetylenic hydrocarbons hydrogenation is combined with a preliminary application of other methods, for example fractionation, in order to reduce the losses of the main products[135,266].

4. CATALYTIC OXIDATION

Thermal oxidation of acetylene requires the use of relatively high temperatures and leads to a complex composition of the reaction products[297]. When the process is carried out in the presence of catalysts[268,269], it is possible to reduce the reaction temperature appreciably and to obtain only carbon dioxide and water as the final oxidation products.

The catalytic oxidation method is most widely used in the removal of acetylene from air in the manufacture of oxygen[9,270-276]. It has proved possible to oxidise acetylene on catalysts at the temperature to which air is heated in compressors for the collection and compression of air (at about 150°C). Catalysts based on silver[9,271,273-276],

manganese[9,270-273], copper[9,270,271,273], palladium, and rhodium[277-279] are the most effective in the oxidation of small amounts of acetylene in air. Manganese ore promoted with silver[280], MnO_2, or Hopcalite[281] are used under industrial conditions. The purification processes are usually carried out at space velocities up to 60 000 h^{-1} and pressures up to 7 atm. After purification the acetylene content in air is 1×10^{-6} vol. % and less.

The method of selective catalytic oxidation is also used for the removal of small amounts of acetylene from certain hydrocarbon mixtures. It has been suggested that gas mixtures with a high ethylene and butadiene content and also hydrocarbon and petroleum cracking gases be freed from an admixture of acetylene using as catalysts metallic copper or CuO on carriers[282-286]. The process is carried out at a temperature of 120–375°C, a space velocity of 100–300 h^{-1}, and in the presence of a 25% excess of oxygen. The purified mixtures virtually do not contain acetylene. However, since the excess oxygen is always consumed in the oxidation of other hydrocarbons, considerable losses of the desired products are observed. In order to improve the selectivity of the purification process, it is recommended that platinum subgroup metals be employed as oxidation catalysts[287-290] and that acetylene be removed with the aid of catalytic solutions or the gas stream be saturated with water vapour. The purification is carried out at 20–300°C and 1–3 atm in the presence of variable-valence metal salts ($CuCl_2$, $FeCl_3$, etc.).

Thus the method of elimination of the acetylene impurity from hydrocarbon systems by its oxidation to carbon dioxide and water requires the employment of expensive catalysts, in particular those based on silver and platinum and also an excess of oxygen, which makes the process liable to risk of explosion and gives rise to considerable losses of the main substance as a result of oxidation.

5. CATALYTIC POLYMERISATION

Several extensive reviews have been published on the condensation and polymerisation reactions of acetylene and its derivatives[26,291,292]. For the purpose under discussion, catalytic methods of polymerising acetylenic hydrocarbons are of interest, since they make it possible to achieve a high degree of process selectivity and high conversions of the acetylenic hydrocarbons. Copper and its compounds have the most intense polymerising effect of acetylenic hydrocarbons.

Recently attempts have been made to employ the capacity of acetylenic hydrocarbons for rapid and easy polymerisation in the elimination of such impurities from various gaseous mixtures. Several procedures for the removal of the acetylenic hydrocarbon impurity from the liquid C_3 fraction[293], the ethane–ethylene fraction[294], olefins[295,296], and products of the oxidative pyrolysis of methane[297] with the aid of aqueous solutions of univalent and bivalent copper have been described. At 60–100°C and in some cases under a high pressure, acetylenic hydrocarbons are converted into liquid and solid polymers, which are separated from the catalytic solution by distillation and filtration. The degree of extraction of the acetylenic hydrocarbons depends markedly on the rate at which the mixture to be purified is passed through the catalytic solution and amounts to not more than 99.6–99.7%. This entails the formation of explosive copper acetylides. In order to improve the process selectivity, it is recommended that acetylenic hydrocarbon be eliminated[294,295] in the presence of oxidants (O_2, air, copper oxides, etc.) capable of maintaining the pH of the solution in the range 1–4.5.

More far-reaching polymerisation of acetylenic hydrocarbons with formation of solid polymers is also employed for the selective removal of the acetylenic hydrocarbon admixture from various hydrocarbon mixtures. In this case the polymerisation products are deposited on the surface of the catalysts and are periodically removed by burning off with an oxygen-containing gas when the catalysts are regenerated. Methods have been patented for the removal of acetylenic hydrocarbons from butadiene[298,299], halogenated olefins[300,302], olefins[299,302-305], and a mixture of olefins and diolefins[306]. The purification processes are usually performed in the gas phase in the temperature range 0–500°C at atmospheric or elevated temperature (up to 35 atm) and a space velocity in the range 500–2500 h^{-1}. Copper and its oxides[298-301,304,305], $CuAl_2O_4$,[302] a catalyst for the cracking of hydrocarbons, for example the aluminosilicate catalyst, deactivated with an alkali metal oxide[303], crystalline zeolites with pore diameters of 6–15 Å and containing between 0.5–12 wt. % of the metal promoting the acetylenic hydrocarbon polymerisation reaction (copper, nickel, cobalt, silver, etc.),[306] and a copper–aluminium alloy with an activated surface[307] are employed as catalysts. As a result of purification, the acetylenic hydrocarbon content decreases in most cases to $(1-5) \times 10^{-4}$ vol. %. It has been stated[298,308] that there are considerable losses (up to 7–12%) of the substances purified in consequence of polymerisation and other reactions on catalysts.

The advantages of the above methods of purification are as follows: elimination of the risk of explosion in the process[300-302,307]; the attainment of exceptionally high selectivity of the catalysts in relation to the polymerisation of acetylenic hydrocarbons to solid polymers[301,302,307]; high efficiency of the elimination of acetylenic hydrocarbons over a wide range of the process parameters and acetylenic hydrocarbon contents in the mixtures purified; ease of regeneration of the catalysts[298-302,304,305,307,308], etc. Therefore, it appears that the method of elimination of acetylenic hydrocarbons from hydrocarbon systems by selective polymerisation to solid polymers is the most convenient, compared with other procedures available, is technologically simplest, and comparatively cheap. It is very promising for the removal of small amounts of acetylenic hydrocarbons from various mixtures, i.e. for a high degree of purification. This is why this method of purification is of considerable practical interest for the large-scale manufacture of monomeric olefins, their halogeno-derivatives, diolefins, and other products, from which very small amounts of acetylenic hydrocarbons must be carefully removed. It is significant that this method is used for the additional purification of the stream of product after the removal of acetylene by selective catalytic hydrogenation.

The present author[309] made for the first time a systematic study of the fair elimination of acetylenic hydrocarbon impurities from hydrocarbon mixtures by the polymerisation method. The catalyst based on the copper spinel of aluminium was recognised as the most effective and promising[302,310]. Therefore all the principal characteristics of the purification and regeneration process were investigated on this catalyst[310,311]. In particular, it was shown that the spinel catalyst has a high mechanical strength and is most promising for continuous purification processes with a stationary bed[311]. A design calculation was made as an example for an industrial purification reactor and the optimum process conditions were selected[312].

6. OTHER METHODS

Apart from the methods discussed, other methods have been proposed for the removal of acetylenic hydrocarbons from various gas mixtures, among which the following may be mentioned.

In order to eliminate 0.1–1.0 vol. % of acetylenic hydrocarbons from a gas, it is mixed with SO_2 to give the proportions SO_2 : acetylenic hydrocarbon = (0.6–2.3) : 1. The resulting mixture is brought into contact at a temperature between −18° and 93°C, a pressure of 0.1–0.4 atm, and a space velocity of 200–1500 h^{-1} with a catalyst consisting of $AgNO_3$ on an inert porous carrier[313].

It is recommended that acetylenic hydrocarbons be removed from vinyl fluoride[314,315], the C_2 fraction[316], and propene[317] by selective hydrochlorination at 100–150°C in the presence of catalysts, for example $HgCl_2$ on activated charcoal. The resulting chloro-derivatives of acetylenic hydrocarbons are readily removed from the mixtures purified by the distillation method. As a result of purification, the acetylenic hydrocarbon content decreases, for example from 1.48 to 0.051 vol. %.

Methods have been described for the removal of acetylenic hydrocarbon impurities from hydrocarbon gases, in particular pyrolytic gas, by amination[318–320]. This method of purification is based on the fact that at an elevated temperature and in the presence of catalysts acetylenic hydrocarbons react with ammonia to form heterocyclic compounds (picolines)[321]. The purification is carried out at 170–400°C using zinc and molybdenum oxides[318,319] or copper(I) chloride[320], all deposited on activated Al_2O_3, as catalysts. For example at 350°C, atmospheric pressure, and a space velocity of 50 h^{-1} in the presence of 10 wt. % NH_3, the content of acetylene in pyrolytic gas decreases from 0.25 to 0.001 vol. %. The ethylenic hydrocarbons present in pyrolytic gas remain unchanged.

The concentration of acetylenic hydrocarbons in the C_4 pyrolytic fraction decreases from 0.03 to 0.007 vol. % when it is passed over an oxide catalyst (Al_2O_3, SiO_2, MgO, or their mixture) with an effective acidity of 1.5–8 at 27 to 120°C.[322] The catalyst must be subjected to a preliminary heat treatment at 480–650°C for 1–24 h.

In order to remove the acetylene impurity from vinyl fluoride[323], the gas mixture is treated with a solution of mercury salts in 10–50% H_2SO_4. Acetylenic hydrocarbons are removed similarly from diolefins[324]. It has also been recommended that mixtures of vinyl fluoride, acetylene, and 1,1-difluoroethane be brominated at 0°C with subsequent distillation of the bromination products[325]. Pure vinyl fluoride is obtained in a yield of about 80% by the debromination of 1,2-dibromo-1-fluoroethane with zinc dust in an alcoholic medium.

IV. ANALYTICAL METHODS FOR THE DETERMINATION OF ACETYLENIC HYDROCARBON IMPURITIES IN VARIOUS MIXTURES

A necessary condition for the further improvement of the methods for the thorough elimination of acetylenic hydrocarbons from various systems is the development of highly sensitive analytical control procedures at the right time. They should make it possible to determine with adequate accuracy the composition of a wide variety of complex mixtures, to estimate quantitatively small amounts of acetylenic hydrocarbon impurities in the mixture, to carry out rapidly large-scale analyses, to achieve a continuous analytical control of the operation of industrial apparatus, and to regulate automatically the course and conditions of technological purification processes. Nowadays various methods are used for this purpose: chemical, physicochemical, and physical.

The characteristic red colour of copper acetylide, obtained in ammonia solutions of copper(I) salts, is used for a qualitative detection of traces of acetylene in various mixtures[102,103,310]. Test papers[104] and also a microchemical method for the determination of acetylene[105] have been developed on this principle. In order to maintain a stable colour of the precipitate for a long time and to increase the sensitivity of the reaction, it is recommended that reducing agents and gelatine be added to the solution. The sensitivity of the freshly prepared reagent with respect to acetylene is 2×10^{-4} vol. %. A method developed for the semiquantitative determination of acetylene in gas mixtures[326] depends on the fact that in the presence of acetylene the yellow colour of the reagent [silica gel impregnated with a mixture of $PdSO_4$ and $(NH_4)_2MoO_4$] becomes yellow-green. The sensitivity of the reagent is 10^{-3} vol. %. Sometimes acetylene is detected in mixtures using the formation of a protective layer on Ag_2CrO_4.[327] When acetylene reacts with Ag_2CrO_4 solution in nitric acid or ammonia, a flakey orange or yellow precipitate is formed. The minimum amount detectable is 1 μg of acetylene.

Among the chemical and physicochemical analytical methods for the quantitative determination of small amounts of acetylenic hydrocarbons, the commonest are absorption, titrimetric, colorimetric, and other methods. The best reagent for the determination of acetylene in hydrocarbon gas mixtures by the volumetric absorption method is an alkaline solution of potassium iodomercurate[328–332]. It has been shown that small amounts of acetylene in oxygen and in air[333] and also in other gases[334] may be determined volumetrically using solutions of copper and silver salts. The acetylene content in concentrated vinyl fluoride has been determined by absorption in bromine water[130]. It is noteworthy that the volumetric method is usually applicable when the content of the acetylenic hydrocarbon is high, i.e. is not less than 0.5%. In this case the error of the determination is ±0.2 abs. %. The use of special apparatus makes it possible to determine from the change in volume even lower concentrations of acetylenic hydrocarbons in the mixture. However the error of the determination then increases appreciably, since the absorption solutions containing copper, silver, and mercury also absorb a certain amount of other components of the mixture analysed (olefins, diolefins, carbon monoxide, molecular oxygen, etc.).

The alkalimetric titration method[335], which depends on the interaction of acetylene and its monosubstituted derivatives with $AgNO_3$ solution followed by titration of the liberated nitric acid with alkali in the presence of a mixed indicator (an alcoholic solution of Methyl Red and Methyl Blue) has been widely adopted in analytical practice for the determination of the overall content of acetylenic hydrocarbons. It is used to determine the admixtures of acetylenic hydrocarbons in ethylene[335], butadiene[14,102], isoprene[336,337], nitrogen and air[338], and also in other mixtures[339–341]. A combined method for the separate determination of acetylene and higher acetylenic hydrocarbons has been described[342,343]. The amount of acetylene is calculated from the weight of the readily crystallisable complex $C_2Ag_2.AgNO_3$ formed when acetylene reacts with a concentrated solution of $AgNO_3$. Higher acetylenes do not form a precipitate. Therefore the overall content

of acetylenic hydrocarbons is found by alkalimetric titration and the content of higher acetylenes is obtained by difference. A method for the determination of small amounts of acetylenic hydrocarbons in gases[103], based on their interaction with an ammoniacal solution of $AgNO_3$ and subsequent titration of the excess $AgNO_3$ with NH_4SCN, has been recommended. Titrimetric methods make it possible to determine the contents of acetylenic hydrocarbons in mixtures to within 5 rel. % with a sensitivity of 10^{-4}%.

Small amounts of acetylene in various gas mixtures are determined successfully with a high accuracy by a colorimetric method[107-111] based on the interaction of acetylene with copper(I) salts in ammoniacal solution. The finely dispersed copper acetylide colours the solution red-violet. Acetylene is determined by colorimetric measurements on the solution against a standard scale[107,108,112-116]. Special apparatus has been designed and methods for the colorimetric determination of acetylene has been improved[117-119]. In some cases[120], in the determination of small amounts of acetylene in air it is sorbed on silica gel at −78°C and the sorbent is then treated with a mixture of an ammoniacal solution of $CuCl_2$ and a solution of $NH_2OH.HCl$. The colour of the silica gel is compared with a standard scale. For this purpose, a linear colour method of determining acetylene in air has been developed[344,345]: air is passed through an indicator tube filled with coarsely porous ShKS silica gel impregnated with potassium iodide; a pale-brown layer is formed in the indicator powder, whose length is proportional to the concentration of acetylene in air. The sensitivity of colorimetric analytical methods is 1×10^{-4}% and the accuracy of the determination is not more than to within 0.05 abs. %.

A polarographic method is used to determine dissolved acetylene[346,347] or its admixtures in gaseous products, for example in chloro-derivatives of ethylene[348,349].

Among physical methods for the analytical determination of acetylenic hydrocarbons in various mixtures and specially pure compounds, gas–liquid partition chromatography has been widely and successfully used. Chromatographic analytical methods have significant advantages over other procedures, namely they are universal, i.e. they yield information about a number of impurities, are very sensitive, rapid, and accurate, it is possible to work with very small samples of materials, the analysis can be automated, etc. Therefore they are the most promising. Numerous studies on the chromatographic analysis of specific systems containing acetylenic hydrocarbon micro-impurities are being systematically published in the periodical literature on science and engineering. Ethylene[350-358], propene[359,360], isobutene and butadiene[14], vinyl fluoride[361,362], vinyl chloride[363-366], pyrolysis gases and the ethylene fraction[367-369], coking gas[370], and other products[371-373] have been analysed by gas–liquid partition chromatography. In most cases apparatus with flame-ionisation or argon detectors is employed. A wide variety of adsorbent, depending on the nature of the products analysed, are used as packing for chromatographic columns. The sensitivity of chromatographic analytical methods with respect to acetylenic hydrocarbons is $10^{-3}-10^{-7}$%, the accuracy of the determination being to within (5–20) rel. %.

Among other physical methods for the analytical determination of acetylenic hydrocarbon impurities, which do not require the separation of the initial mixtures into components, certain spectroscopic procedures are employed. Infrared spectroscopic data are used to determine the purity of ethylene and the content of acetylenic hydrocarbons in ethylene[374,375], vinyl fluoride[376], and other mixtures[377-379]. Certain improved analytical techniques have been proposed[380]. The sensitivity of the method is 4×10^{-3} vol. % and the accuracy of the determination is to within 10 rel. %. Attempts have been made to employ the mass-spectrometric method for the analysis of certain mixtures, for example coking gas[381] and the gases in the synthesis of vinyl fluoride[382] in order to determine the acetylenic hydrocarbon impurity. However, isomeric hydrocarbons and compounds with the same number of carbon atoms in the molecule are difficult to determine by the mass-spectrometric procedure. In the analysis of complex mixtures, the sensitivity and accuracy of this method are greatly impaired. A combination of the gas–liquid chromatographic and mass-spectrometric methods appears promising[383].

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